### IN THE CLAIMS:

## Claims 1-12. (canceled)

\ \_13. (original) A chiral chelating agent having a formula (13) as follows and an enantiomeric isomer thereof:

wherein n is an integer between 0 and 4.

2.14. (original) A chiral chelating agent having a formula (14) as follows and an enantiomeric isomer thereof:

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wherein n is an integer between 0 and 4.

15. (original) A chiral chelating agent having a formula (15) as follows and an enantiomeric isomer thereof:

wherein n is an integer between 0 and 4.

(currently amended) A chiral chelating agent having a formula (16) as follows and an a

diastereomeric or an enantiomeric isomer thereof:

wherein X represents an oxygen atom or a nitrogen atom; R<sup>1</sup>, R<sup>2</sup> R<sup>3</sup> and R<sup>4</sup> represent H, methyl, ethyl, a primary, secondary or tertiary straight, branched or cyclic alkyl group having 3-7 carbon atoms, a heterocyclic or aromatic group, an aromatic group substituted at the 2-, 3- or 4-position, an aromatic-like group, a naphthyl or naphthyl-derived group or the above groups substituted with at least a halogen.

Claims 17-23. (canceled)

### IN THE CLAIMS:

Claims 1-12. (canceled)

13. (original) A chiral chelating agent having a formula (13) as follows and an enantiomeric isomer thereof:

$$\begin{array}{c}
M_{\Theta} & M_{\Theta} \\
N - (CH_2)_n - N
\end{array}$$

$$\begin{array}{c}
N \\
M_{\Theta}
\end{array}$$

wherein n is an integer between 0 and 4.

14. (original) A chiral chelating agent having a formula (14) as follows and an enantiomeric isomer thereof:

wherein n is an integer between 0 and 4.

15. (original) A chiral chelating agent having a formula (15) as follows and an enantiomeric isomer thereof:

wherein n is an integer between 0 and 4.

16. (currently amended) A chiral chelating agent having a formula (16) as follows and an a

diastereomeric or an enantiomeric isomer thereof:

wherein X represents an oxygen atom or a nitrogen atom; R<sup>1</sup>, R<sup>2</sup> R<sup>3</sup> and R<sup>4</sup> represent H, methyl, ethyl, a primary, secondary or tertiary straight, branched or cyclic alkyl group having 3-7 carbon atoms, a heterocyclic or aromatic group, an aromatic group substituted at the 2-, 3- or 4-position, an aromatic-like group, a naphthyl or naphthyl-derived group or the above groups substituted with at least a halogen.

Claims 17-23. (canceled)



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FILE PREGISTERY ENTERED AT 13:25:40 ON 10 DEC 2004 L5 A1 SIZA LA

FILES WELX ENTERED AT 13:25:42 ON 10 DEC 2004 1 US20040176243/PN E TW2003-92104138/AP, PRN E TW2003-104138/AP, PRN 1 TW2003-104138/AP, PRN

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FILE COVERS 1907 - 10 Dec 2004 VOL 141 ISS 25 FILE LAST UPDATED: 9 Dec 2004 (20041209/ED)

This file contains CAS Reqistry Numbers for easy and accurate substance identification.

## es d'all law

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ΑN
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DN
     141:243058
     Entered STN: 10 Sep 2004
ED
     Preparation of chiral chelating agent and chiral catalysts for
TΙ
     stereoselective addition reactions
IN
     Chen, Kwunmin; Yang, Kung-shou; Lee, Wei-der; Pan, Jia-fu
PΑ
     Taiwan
     U.S. Pat. Appl. Publ., 11 pp.
so
     CODEN: USXXCO
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     Patent
     English
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IC
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     502162000; 556032000; 546002000; 548101000; 564147000
NCL
CC
     23-17 (Aliphatic Compounds)
     Section cross-reference(s): 30, 78
FAN.CNT 1
     PATENT NO.
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DATE PI US 2004176243 QRAMBIW 2003 9210413 US 2003-612609 M120030701133-1-7 20040909 A1 20030227 CLASS

PATENT NO. CLASS PATENT FAMILY CLASSIFICATION CODES US 2004176243 ICM C07F001-00

ICS B01J031-00

NCL 502162000; 556032000; 546002000; 548101000; 564147000

OS MARPAT 141:243058

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$$CO_2R$$
  $N-(CH_2)_{11}-N$   $CO_2R$   $OH$   $CO_2R^2$   $R^1$   $CO_2R^2$   $R^2$   $CO_2R^2$   $CO_2R^2$ 

Chiral chelating agents and chiral catalysts, e.g. I (R = H, Me, Et, primary, secondary or tertiary straight, branched or cyclic C3-7 alkyl; heterocyclic, (un)substituted aromatic, aromatic-like, naphthyl, or naphthyl-derived group; n = 0-4) which are formed from the chiral chelating agents and metal, are described. Thus I (n = 2, R = H) was prepared by condensation of (+)-ketopinic acid with ethylenediamine in CHCl3. The complex of I (n = 2, R = H) with La(OTf)3 was screened as catalysts for the asym. Baylis-Hillman reaction of aldehydes R1CHO (R1 = Ph, Me, Et, Me2CH, 4-MeOC6H4, 4-O2NC6H4, cyclohexyl, PhCH2CH2CH2) and acrylate esters H2C:CHCO2R2 (R2 = Me, CMe3, Ph, CH2Ph, 1-naphthyl) to give (S)-alcs. II in 35-97% yields and 6-95% e.e.

ST stereoselective Baylis Hillman reaction chiral chelating agent catalyst; lanthanide camphor deriv catalyst prepn stereoselective addn reaction; aldehyde stereoselective addn acrylate chiral lanthanide catalyst; ketopinic acid condensation diamine

T Addition reaction

Addition reaction catalysts

(Baylis-Hillman, stereoselective; preparation of chiral chelating agent and chiral catalysts for stereoselective addition reactions)

IT Cycloaddition reaction

Cycloaddition reaction catalysts

(aziridination, stereoselective; preparation of chiral chelating agent and chiral catalysts for stereoselective reactions)

IT Asymmetric synthesis and induction

(preparation of chiral chelating agent and chiral catalysts for stereoselective addition reactions)

IT Aldehydes, reactions

RL: RCT (Reactant); RACT (Reactant or reagent)

(preparation of chiral chelating agent and chiral catalysts for stereoselective addition reactions)

IT Cyclopropanation

(preparation of chiral chelating agent and chiral catalysts for stereoselective reactions)

IT Cycloaddition reaction

Cycloaddition reaction catalysts

(stereoselective; preparation of chiral chelating agent and chiral catalysts for multiple types of stereoselective cycloaddn. reactions)

IT Addition reaction

Addition reaction catalysts

(stereoselective; preparation of chiral chelating agent and chiral catalysts for stereoselective addition reactions)

IT Aldol condensation

Aldol condensation catalysts

Amination

Amination catalysts

Aminohydroxylation

Aminohydroxylation catalysts

Cyclopropanation catalysts

Hydrogenation

Hydrogenation catalysts

Michael reaction

Michael reaction catalysts

Reduction

Reduction catalysts

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(stereoselective; preparation of chiral chelating agent and chiral catalysts
        for stereoselective reactions)
     52093-25-1, Europium triflate
54761-04-5, Ytterbium triflate
IT
                                       52093-26-2. Lanthanum triflate
     RL: CAT (Catalyst use); USES (Uses)
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     404582-34-9P 423770-46-1P
TT
     RL: CAT (Catalyst use); PRP (Properties); SPN (Synthetic preparation);
     PREP (Preparation); USES (Uses)
        (preparation of chiral chelating agent and chiral catalysts for
        stereoselective addition reactions)
     404582-36-1P 423770-45-0P
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        (preparation of chiral chelating agent and chiral catalysts for
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IT
     75-07-0, Acetaldehyde, reactions
                                          78-84-2, Isobutyraldehyde
                                                                       96-33-3.
     Methyl acrylate 100-52-7, Benzaldehyde, reactions 107-15-3,
     Ethylenediamine, reactions 123-11-5, 4-Methoxybenzaldehyde, reactions 123-38-6, Propionaldehyde, reactions 555-16-8, 4-Nitrobenzaldehyde, reactions 937-41-7, Phenyl acrylate 1121-22-8, (.+-.)-trans-1,2-
                          1663-39-4, tert-Butyl acrylate
     Diaminocyclohexane
                                                             2043-61-0,
     Cyclohexanecarboxaldehyde 2495-35-4, Benzyl acrylate
                                                                18328-11-5,
     4-Phenylbutanal 20069-66-3 40724-67-2, (+)-Ketopinic acid
     RL: RCT (Reactant); RACT (Reactant or reagent)
         (preparation of chiral chelating agent and chiral catalysts for
        stereoselective addition reactions)
                    112572-93-7P
                                                                     221346-91-4P
     108945-27-3P
                                    140238-43-3P
                                                     189372-86-9P
                     500166-63-2P
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     RL: SPN (Synthetic preparation); PREP (Preparation)
        (preparation of chiral chelating agent and chiral catalysts for
        stereoselective addition reactions)
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COPYRIGHT (C) 2004 THE THOMSON CORPORATION
FILE LAST UPDATED:
                              8 DEC 2004
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MOST RECENT DERWENT UPDATE:
                                 200479
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>>> FOR DETAILS OF THE PATENTS COVERED IN CURRENT UPDATES, SEE
    http://thomsonderwent.com/coverage/latestupdates/
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>>> SMILES and ISOSMILES strings are no longer available as
    Derwent Chemistry Resource display fields <<<
     ANSWER 1 OF 1 WPIX COPYRIGHT 2004 THE THOMSON CORP on STN
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                        WPIX
DNC
     C2004-230782
     New chiral chelating agents useful as catalyst in e.g. chiral alkylation,
TI
     reduction, Michael addition or Baylis-Hillman reaction.
DC
IN
     CHEN, K; LEE, W; PAN, J; YANG, K
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PA
      (CHEN-I) CHEN K; (LEEW-I) LEE W; (PANJ-I) PAN J; (YANG-I) YANG K
CYC 1
PI US 2002176243 AL 200710209 (200462) AT US 2004176243 Al US 2003 612609 20030701 PRAI EW 2008 200408 20080227 IC ICM C07F001-00
           C07F001-00
IC
     ICS B01J031-00
     US2004176243 A UPAB: 20040928
     NOVELTY - Chiral chelating agents are new.
           DETAILED DESCRIPTION - Chiral chelating agents of formulae (I) - (IX)
     are new.
           R1, R2 and R = H or T;
     T = methyl, ethyl, primary, secondary or tertiary straight, branched or cyclic 3-7C alkyl, heterocyclic group, aromatic group (optionally
     substituted at 2-,3- or 4-positions), an aromatic-like group, naphthyl or
     naphthyl-derived group;
          R asterisk 1-R asterisk 4 = T (optionally substituted by at least a
     halo) or H;
     X = 0 or N; and
           R3 = CONR1R2, COOR or CH2SO2NR1R2.
           An INDEPENDENT CLAIM is included for a chiral catalyst obtained from
     the chiral chelating agent of formulae (I) - (IX) and a metal.
           USE - As catalysts in chiral (di)alkylation, reduction, cyclization
     including (2+2), (3+2), (4+2) or (2+2+2) cyclization, hydrogenation,
     epoxidation, cyclization of propane, aziridination, amination, an Aldol
     reaction, Michael addition reaction or Baylis-Hillman reaction (claimed).
           {\tt ADVANTAGE} - The chiral chelating agents improve the
     enantioselectivity and reduces the reaction time of the catalytic
     Baylis-Hillman reaction.
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     AB; GI; DCN
FA
     CPI: E05-A; E05-B; E05-P; E06-H; E07-H; E10-A08C; E10-A19B; E10-A20B;
MC
           E10-B01C; E10-B01E; E10-D03A; E10-D03D; E10-G02A2; N01-A; N01-B; N02;
           N03; N05-B; N05-C
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Property values tagged with IC are from the ZIC/VINITI data file provided by InfoChem.

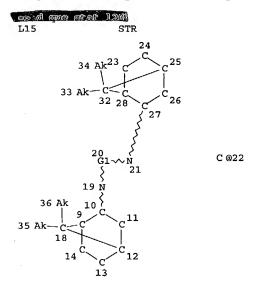
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TSCA INFORMATION NOW CURRENT THROUGH MAY 21, 2004

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Experimental and calculated property data are now available. For more information enter HELP PROP at an arrow prompt in the file or refer to the file summary sheet on the web at: http://www.cas.org/ONLINE/DBSS/registryss.html



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GRAPH ATTRIBUTES: RING(S) ARE ISOLATED OR EMBEDDED NUMBER OF NODES IS 22

STEREO ATTRIBUTES: NONE

L17 68 SEA FILE=REGISTRY SSS FUL L15

L18 STR

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NSPEC IS RC AT 22

DEFAULT MLEVEL IS ATOM
DEFAULT ECLEVEL IS LIMITED

GRAPH ATTRIBUTES:

RING(S) ARE ISOLATED OR EMBEDDED

NUMBER OF NODES IS 22

STEREO ATTRIBUTES: NONE

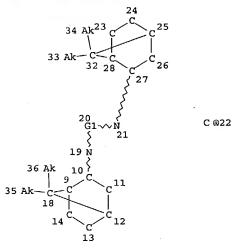
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SEARCH TIME: 00.00.01







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DEFAULT MLEVEL IS ATOM

DEFAULT ECLEVEL IS LIMITED

GRAPH ATTRIBUTES:

RING(S) ARE ISOLATED OR EMBEDDED

NUMBER OF NODES IS 22

STEREO ATTRIBUTES: NONE

68 SEA FILE=REGISTRY SSS FUL L15 L17 STR

L23

NODE ATTRIBUTES:

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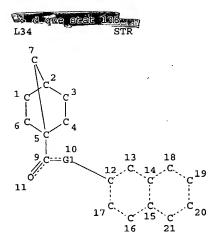
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100.0% PROCESSED SEARCH TIME: 00.00.01 30 ITERATIONS





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GRAPH ATTRIBUTES: RING(S) ARE ISOLATED OR EMBEDDED NUMBER OF NODES IS 20

STEREO ATTRIBUTES: NONE

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               1 TW2003-92104138/AP, PRN
L3
               1 L1-2
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 L5
              41 SEA L4
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L16
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 L19
               2 L18 SAM SUB=L17
          SAVE TEMP L20 KUMAR609SO/A
120 17
L21
                 STR L15
 L22
              16 L5 AND NR>1
                 STR L21
 L23
L24 1 L23 SAM SUB=L17
L25 15 L23 BUND SUB=C17
SAVE TEMP L25 KUMAR609S1/A
 L26
              46 L20 OR L25
 L27
                 STR
               0 L27
L28
               7 L22 AND C6-C6/ES
L29
 L30
                 STR L27
               0 L30
 L31
 L32
                 STR L30
               0 L32
 L33
 L34
                 STR L32
 L35
               1 L34
              13 LE34: PUIGN
SAVE TEMP KUMAR609F1/A L36
4436
     EDDE HEADLUSY ENTERED AT 14:31:00 ON 10 DEC 2004
 L37
               5 L36
 L38
                 E CHEN K/AU
 T.39
            1691 E3-35
                 E CHEN KWUNMIN/AU
 L40
              27 E3
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E YANG K/AU

E YANG KUNG/AU

253 E3,E19

12 E7-8

L41

L42

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E LEE W/AU

L43 308 E3,E13
E LEE WEI/AU

L44 43 E3,E10
E PAN J/AU

L45 227 E3,E8
E PAN JIA/AU

L46 7 E3,E6
L47 808 (TAIWAN (1A) NORMAL)/CS,PA

148 37 L87 38 NOR LASS
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=> b hcap

PRICE VHCARUSA ENTERED AT 14:37:15 ON 10 DEC 2004
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FILE COVERS 1907 - 10 Dec 2004 VOL 141 ISS 25 FILE LAST UPDATED: 9 Dec 2004 (20041209/ED)

This file contains CAS Registry Numbers for easy and accurate substance identification.

### sa dealth fhitstr 148 tot

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ANSWER 1 OF 3 HCAPLUS COPYRIGHT 2004 ACS on STN
     2004:739941 HCAPLUS
\mathbf{A}\mathbf{N}
DN
     141:243058
ED
     Entered STN: 10 Sep 2004
ΤI
     Preparation of chiral chelating agent and chiral catalysts for
     stereoselective addition reactions
(hen, Kwunmin, Yang, Kung-show Mee, Wede dern,
Ran, Marfu)
IN
PA
     Taiwan
so
     U.S. Pat. Appl. Publ., 11 pp.
     CODEN: USXXCO
DT
     Patent
     English
LA
     ICM C07F001-00
IC
     ICS B01J031-00
     502162000; 556032000; 546002000; 548101000; 564147000
     23-17 (Aliphatic Compounds)
     Section cross-reference(s): 30, 78
FAN.CNT 1
     PATENT NO.
                           KIND
                                                APPLICATION NO.
                                                                         DATE
     US 2004176243
                                   20040909
                            A1
                                                US 2003-612609
                                                                         20030701
PRAI TW 2003-92104138
                            Α
                                   20030227
CLASS
                  CLASS PATENT FAMILY CLASSIFICATION CODES
 PATENT NO.
                          C07F001-00
 US 2004176243
                  ICM
                  ICS
                          B01J031-00
                  NCL
                          502162000; 556032000; 546002000; 548101000; 564147000
     MARPAT 141:243058
GI
```

Me Me 
$$CO_2R$$
  $N-(CH_2)_{11}-N$   $CO_2R$   $OH$   $R^1$   $CO_2R^2$   $Me$   $Me$   $I$   $CH_2$   $II$ 

Chiral chelating agents and chiral catalysts, e.g. I (R = H, Me, Et, primary, secondary or tertiary straight, branched or cyclic C3-7 alkyl; heterocyclic, , (un) substituted aromatic, aromatic-like, naphthyl, or naphthyl-derived group; n=0-4) which are formed from the chiral chelating agents and metal, are described. Thus I (n=2, R = H) was prepared by condensation of (+)-ketopinic acid with ethylenediamine in CHCl3. The complex of I (n=2, R=H) with La(OTf)3 was screened as catalysts for the asym. Baylis-Hillman reaction of aldehydes R1CHO (R1 = Ph, Me, Et, Me2CH, 4-MeOC6H4, 4-O2NC6H4, cyclohexyl, PhCH2CH2CH2) and acrylate esters H2C:CHCO2R2 (R2 = Me, CMe3, Ph, CH2Ph, 1-naphthyl) to give (S)-alcs. II in 35-97% yields and 6-95% e.e.

ST stereoselective Baylis Hillman reaction chiral chelating agent catalyst; lanthanide camphor deriv catalyst prepn stereoselective addn reaction; aldehyde stereoselective addn acrylate chiral lanthanide catalyst; ketopinic acid condensation diamine

Addition reaction

Addition reaction catalysts

(Baylis-Hillman, stereoselective; preparation of chiral chelating agent and chiral catalysts for stereoselective addition reactions)

Cycloaddition reaction

Cycloaddition reaction catalysts

(aziridination, stereoselective; preparation of chiral chelating agent and chiral catalysts for stereoselective reactions)

Asymmetric synthesis and induction IT

(preparation of chiral chelating agent and chiral catalysts for stereoselective addition reactions)

TT Aldehydes, reactions

RL: RCT (Reactant); RACT (Reactant or reagent)

(preparation of chiral chelating agent and chiral catalysts for stereoselective addition reactions)

IT Cyclopropanation

(preparation of chiral chelating agent and chiral catalysts for stereoselective reactions)

Cycloaddition reaction

Cycloaddition reaction catalysts

(stereoselective; preparation of chiral chelating agent and chiral catalysts for multiple types of stereoselective cycloaddn. reactions)

IT Addition reaction

Addition reaction catalysts

(stereoselective; preparation of chiral chelating agent and chiral catalysts for stereoselective addition reactions)

IT Aldol condensation

Aldol condensation catalysts

Amination

Amination catalysts

Aminohydroxylation

Aminohydroxylation catalysts

Cyclopropanation catalysts

Hydrogenation

Hydrogenation catalysts

Michael reaction

Michael reaction catalysts

Reduction

Reduction catalysts

(stereoselective; preparation of chiral chelating agent and chiral catalysts for stereoselective reactions)

52093-25-1, Europium triflate 52093-26-2, Lanthanum triflate

54761-04-5, Ytterbium triflate

RL: CAT (Catalyst use); USES (Uses)

(preparation of chiral chelating agent and chiral catalysts for

```
stereoselective addition reactions)
IT
     404582-34-9P 423770-46-1P
     RL: CAT (Catalyst use); PRP (Properties); SPN (Synthetic preparation);
     PREP (Preparation); USES (Uses)
        (preparation of chiral chelating agent and chiral catalysts for
        stereoselective addition reactions)
TT
     404582-36-1P 423770-45-0P
     RL: CAT (Catalyst use); SPN (Synthetic preparation); PREP (Preparation);
     USES (Uses)
        (preparation of chiral chelating agent and chiral catalysts for
        stereoselective addition reactions)
IT
     75-07-0, Acetaldehyde, reactions 78-84-2, Isobutyraldehyde
     Methyl acrylate 100-52-7, Benzaldehyde, reactions 107-15-3, Ethylenediamine, reactions 123-11-5, 4-Methoxybenzaldehyde, reactions
     123-38-6, Propionaldehyde, reactions 555-16-8, 4-Nitrobenzaldehyde, reactions 937-41-7, Phenyl acrylate 1121-22-8, (.+-.)-trans-1,2-
     Diaminocyclohexane 1663-39-4, tert-Butyl acrylate 2043-61-0,
     Cyclohexanecarboxaldehyde 2495-35-4, Benzyl acrylate
                                                                 18328-11-5.
     4-Phenylbutanal 20069-66-3 40724-67-2, (+)-Ketopinic acid
     RL: RCT (Reactant); RACT (Reactant or reagent)
         (preparation of chiral chelating agent and chiral catalysts for
        stereoselective addition reactions)
TT
     108945-27-3P
                     112572-93-7P
                                     140238-43-3P
                                                     189372-86-9P
                                                                      221346-91-4P
     293307-67-2P
                     500166-63-2P
                                     500166-64-3P
                                                     500166-65-4P
                                                                      500166-66-5P
     500166-67-6P
                     500166-68-7P
                                     500166-69-8P
                                                      500166-70-1P
                                                                      500166-71-2P
     500166-72-3P
                     500166-73-4P
                                     753007-96-4P
     RL: SPN (Synthetic preparation); PREP (Preparation)
        (preparation of chiral chelating agent and chiral catalysts for
        stereoselective addition reactions)
IT
     423770-46-1P
     RL: CAT (Catalyst use); PRP (Properties); SPN (Synthetic preparation);
     PREP (Preparation); USES (Uses)
        (preparation of chiral chelating agent and chiral catalysts for
        stereoselective addition reactions)
RN
     423770-46-1 HCAPLUS
     Bicyclo [2.2.1] heptane-1-carboxylic acid, 2,2'-azinobis [7,7-dimethyl-,
     (1S,1'S,4R,4'R) - (9CI) (CA INDEX NAME)
```

Absolute stereochemistry.

Double bond geometry unknown.

```
L48
     ANSWER 2 OF 3 HCAPLUS COPYRIGHT 2004 ACS on STN
     2002:977476 HCAPLUS
AN
DN
     138:204497
     Entered STN: 29 Dec 2002
ED
TТ
     Chiral Lewis Acid-Catalyzed Asymmetric Baylis-Hillman Reactions
   Mang, Kung Shuo, Lee Walloor, Pank Walland:
Chan, Kwinmin
Department of Chemistry, National Taiwan Normal
University, Taipei, 116, Taiwan
AU
CS
SO
     Journal of Organic Chemistry (2003), 68(3), 915-919
     CODEN: JOCEAH; ISSN: 0022-3263
     American Chemical Society
PB
DT
     Journal
T.A
     English
     21-2 (General Organic Chemistry)
CC
     Section cross-reference(s): 75
     CASREACT 138:204497
     An effective chiral Lewis acid-catalyzed asym. Baylis-Hillman reaction is
     described. Good to high enantioselectivities were obtained using 3 mol %
     chiral catalyst. Novel camphor-derived dimerized ligands were prepared from
     the condensation of (+)-ketopinic acid with diamines and hydrazine under
     acidic conditions. When .alpha.-naphthyl acrylate was used as a Michael
     acceptor, the reaction is complete within 20 min with high
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Kumar 10/612609

Page 8

stereoselectivity and in reasonable chemical yields. STBaylis Hillman asym chiral Lewis acid catalyst Addition reaction (Baylis-Hillman, stereoselective; chiral Lewis acid-catalyzed asym. Baylis-Hillman reactions) TT Asymmetric synthesis and induction (chiral Lewis acid-catalyzed asym. Baylis-Hillman reactions) IT Lewis acids RL: CAT (Catalyst use); USES (Uses) (chiral Lewis acid-catalyzed asym. Baylis-Hillman reactions) Ligands RL: CAT (Catalyst use); SPN (Synthetic preparation); PREP (Preparation); USES (Uses) (chiral; chiral Lewis acid-catalyzed asym. Baylis-Hillman reactions) TT Addition reaction catalysts (stereoselective, Baylis-Hillman; chiral Lewis acid-catalyzed asym. Baylis-Hillman reactions) IT 52093-26-2, Lanthanum(III) triflate RL: CAT (Catalyst use); USES (Uses) (chiral Lewis acid-catalyzed asym. Baylis-Hillman reactions) 500224-32-8P 500224-33-9P RL: CAT (Catalyst use); SPN (Synthetic preparation); PREP (Preparation); USES (Uses) (chiral Lewis acid-catalyzed asym. Baylis-Hillman reactions) 75-07-0, Acetaldehyde, reactions 78-84-2, Isobutyraldehyde 100-52-7, Benzaldehyde, reactions Methyl acrylate 104-53-0 3-Phenylpropanal 107-15-3, Ethylenediamine, reactions 123-11-5, p-Anisaldehyde, reactions 123-38-6, Propionaldehyde, reactions 555-16-8, 4-Nitrobenzaldehyde, reactions 937-41-7, Phenyl acrylate 1121-22-8, trans-1,2-Cyclohexanediamine 1663-39-4, tert.-Butyl acrylate 2043-61-0, Cyclohexanecarboxaldehyde 2495-35-4, Benzyl acrylate 20069-66-3, 1-Naphthyl acrylate 40724-67-2, (+)-Ketopinic acid RL: RCT (Reactant); RACT (Reactant or reagent) (chiral Lewis acid-catalyzed asym. Baylis-Hillman reactions) 500166-64-3P 500166-69-8P 500166-70-1P RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent) (chiral Lewis acid-catalyzed asym. Baylis-Hillman reactions) 108945-27-3P 112572-93-7P 140238-43-3P 140630-33-7P 189372-86-9P 500166-63-2P 221346-91-4P 293307-67-2P 500166-65-4P 500166-66-5P 500166-67-6P 500166-68-7P 500166-71-2P 500166-72-3P 500166-73-4P 500166-75-6P 500166-76-7P 500166-74-5P RL: SPN (Synthetic preparation); PREP (Preparation) (chiral Lewis acid-catalyzed asym. Baylis-Hillman reactions) 500224-34-0P 500224-35-1P RL: CAT (Catalyst use); PRP (Properties); SPN (Synthetic preparation); PREP (Preparation); USES (Uses) (crystal structure of) RE.CNT THERE ARE 27 CITED REFERENCES AVAILABLE FOR THIS RECORD (1) Aggarwal, V; J Chem Soc, Chem Commun 1996, P2713 HCAPLUS
 (2) Aggarwal, V; J Org Chem 1998, V63, P7183 HCAPLUS (3) Barrett, A; J Chem Soc Chem Commun 1998, P2533 HCAPLUS (4) Barrett, A; J Chem Soc, Chem Commun 1995, P1755 HCAPLUS (5) Basavaiah, D; Tetrahedron 1996, V52, P8001 HCAPLUS (6) Brzezinski, L; J Am Chem Soc 1997, V119, P4317 HCAPLUS (7) Ciganek, E; Org React 1997, V51, P201 HCAPLUS (8) Corey, E; J Am Chem Soc 1994, V116, P3611 HCAPLUS (9) Drewes, S; Tetrahedron 1988, V44, P4653 HCAPLUS (10) Drewes, S; Tetrahedron:Asymmetry 1992, V3, P255 HCAPLUS (11) Hahn, F; Chem Ber 1990, V123, P481 HCAPLUS (12) Hayase, T; J Chem Soc, Chem Commun 1998, P1271 HCAPLUS (13) Ishihara, K; J Org Chem 2000, V65, P9125 HCAPLUS (14) Iwabuchi, Y; Am Chem Soc 1999, V121, P10219 HCAPLUS (15) Iwabuchi, Y; Chem Commun 2001, P2030 HCAPLUS (16) Iwabuchi, Y; Tetrahedron Lett 2001, V42, P7867 HCAPLUS (17) Kundig, E; Tetrahedron Lett 1993, V34, P7049 (18) Langer, P; Angew Chem, Int Ed 2000, V39, P3049 HCAPLUS (19) Lee, W; Chem Commun 2001, P1612 HCAPLUS (20) Noyori, R; Asymmetric Catalysis in Organic Synthesis 1994 (21) Oishi, T; Tetrahedron: Asymmetry 1995, V6, P1241 HCAPLUS (22) Ojima, I; Catalytic Asymmetric Synthesis 1993 (23) Pan, J; J Mol Catal A: Chem 2001, V176, P19 HCAPLUS (24) Sartor, D; Synlett 1990, P197 HCAPLUS (25) Takasu, M; Synlett 1990, P194 HCAPLUS (26) Yang, K; Org Lett 2000, V2, P729 HCAPLUS

Absolute stereochemistry.

Double bond geometry as shown.

```
ANSWER 3 OF 3 HCAPLUS COPYRIGHT 2004 ACS on STN
L48
     2002:173335 HCAPLUS
AN
DN
     136:369559
                   11 Mar 2002
ED
     Entered STN:
     Enantioselective Aziridination of Alkenes with N-Aminophthalimide in the
TI
     Presence of Lead Tetraacetate-Mediated Chiral Ligand
   wang, Kung Shou, Kehen, Kwunmun a
Department of Chemistry, National Sakwan Normal
Lightversity, Taipei, 116, Taiwan
AU
CS
SO
     Organic Letters (2002), 4(7), 1107-1109
     CODEN: ORLEF7; ISSN: 1523-7060
PB
     American Chemical Society
DT
     Journal
T.A
     English
CC
     27-3 (Heterocyclic Compounds (One Hetero Atom))
os
     CASREACT 136:369559
     Reaction of various N-alkenoyloxazolidinones with N-aminophthalimide and
AB
     lead tetraacetate in the presence of camphor-derived chiral ligands
     provides the desired N-phthalimidoaziridines in good to high enantiomeric
     excess (67-95% ee) at 0 .degree.C within 15 min. The absolute stereochem. of
     the corresponding aziridine derivs. was established by chemical correlations.
ST
     aziridination stereoselective alkenoyloxazolidinone aminophthalimide
     chiral ligand
IT
     Cycloaddition reaction
     Cycloaddition reaction catalysts
        (aziridination, stereoselective; enantioselective aziridination of
        alkenes with N-aminophthalimide in the presence of lead tetraacetate
        and a chiral ligand)
IT
     Ligands
     RL: CAT (Catalyst use); SPN (Synthetic preparation); PREP (Preparation);
     USES (Uses)
        (chiral; enantioselective aziridination of alkenes with
        N-aminophthalimide in the presence of lead tetraacetate and a chiral
        ligand)
     Alkenes, reactions
     RL: RCT (Reactant); RACT (Reactant or reagent)
        (enantioselective aziridination of alkenes with N-aminophthalimide in
        the presence of lead tetraacetate and a chiral ligand)
     87-69-4, (+)-Tartaric acid, uses
                                         546-67-8, Lead tetraacetate
IT
     RL: CAT (Catalyst use); USES (Uses)
        (enantioselective aziridination of alkenes with N-aminophthalimide in
        the presence of lead tetraacetate and a chiral ligand)
IT
     404582-34-9P
                    404582-36-1P 423770-45-0P 423770-46-1P
     RL: CAT (Catalyst use); SPN (Synthetic preparation); PREP (Preparation);
     USES (Uses)
        (enantioselective aziridination of alkenes with N-aminophthalimide in
        the presence of lead tetraacetate and a chiral ligand)
IT
     423770-47-2P
     RL: PRP (Properties); RCT (Reactant); SPN (Synthetic preparation); PREP
     (Preparation); RACT (Reactant or reagent)
        (enantioselective aziridination of alkenes with N-aminophthalimide in
                                        Search done by Noble Jarrell
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(CA INDEX

the presence of lead tetraacetate and a chiral ligand) IT 423770-56-3P RL: PRP (Properties); SPN (Synthetic preparation); PREP (Preparation) (enantioselective aziridination of alkenes with N-aminophthalimide in the presence of lead tetraacetate and a chiral ligand) TT 107-15-3, Ethylenediamine, reactions 464-78-8, Ketopinic acid 2043-21-2 20439-47-8, (1R,2R)-1,2-Cyclohexanediamine 21436-03-3, 31978-13-9 (1S,2S)-1,2-Cyclohexanediamine 109299-92-5 109299-93-6 109299-94-7 227024-93-3 423770-49-4 RL: RCT (Reactant); RACT (Reactant or reagent) (enantioselective aziridination of alkenes with N-aminophthalimide in the presence of lead tetraacetate and a chiral ligand) 423770-51-8P RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent) (enantioselective aziridination of alkenes with N-aminophthalimide in the presence of lead tetraacetate and a chiral ligand) IT 1875-48-5, N-Aminophthalimide RL: RGT (Reagent); RACT (Reactant or reagent) (enantioselective aziridination of alkenes with N-aminophthalimide in the presence of lead tetraacetate and a chiral ligand) 151-56-4DP, Aziridine, derivs. 332923-24-7P 332923-28-1P 423770-52-9P 423770-53-0P 423770-54-1P 423770-48-3P 423770-50-7P 423770-55-2P RL: SPN (Synthetic preparation); PREP (Preparation) (enantioselective aziridination of alkenes with N-aminophthalimide in the presence of lead tetraacetate and a chiral ligand) RE.CNT THERE ARE 1 CITED REFERENCES AVAILABLE FOR THIS RECORD RE(1) Yang, K; J Org Chem 2001, V66, P1676 HCAPLUS 423770-45-0P RL: CAT (Catalyst use); SPN (Synthetic preparation); PREP (Preparation); USES (Uses) (enantioselective aziridination of alkenes with N-aminophthalimide in the presence of lead tetraacetate and a chiral ligand) RN 423770-45-0 HCAPLUS Bicyclo[2.2.1]heptane-1-carboxylic acid, 2,2'-(1,2-CN

Absolute stereochemistry. Double bond geometry unknown.

NAME)

$$\begin{array}{c|c} R \\ \text{Me} \\ \hline \\ S \\ CO_2H \\ \end{array}$$

### =>46 and hintener alay took

- ANSWER 1 OF 27 HCAPLUS COPYRIGHT 2004 ACS on STN 2003:405897 HCAPLUS AN
- DN 139:230450
- ED Entered STN: 28 May 2003
- Synthesis of C2-symmetrical diamine based on (1R)-(+)-camphor and TI application to oxidative aryl coupling of naphthols

ethanediyldinitrilo)bis[7,7-dimethyl-, (1S,1'S,4R,4'R)- (9CI)

- Caselli, Alessandro; Giovenzana, Giovanni B.; Palmisano, Giovanni; Sisti, ΑU
- Massimo; Pilati, Tullio Dipartimento di Chimica Organica e Industriale, Universita degli Studi di CS Milano, Milan, I-20133, Italy
- Tetrahedron: Asymmetry (2003), 14(11), 1451-1454 CODEN: TASYE3; ISSN: 0957-4166
- PB Elsevier Science B.V.
- DT Journal
- English
- CC 25-24 (Benzene, Its Derivatives, and Condensed Benzenoid Compounds)
- CASREACT 139:230450 os
- AB The new C2-sym. 1,2-diamine {N,N'-bis[(1R,2R,4R)-1,7,7-

Kumar 10/612609

Page 11

trimethylbicyclo[2.2.1]hept-2-yl]-1,2-ethanediamine} (I) was synthesized from com. (1R)-(+)-camphor and scrutinized as ligand in the oxidative biaryl coupling of naphthol derivs. Under the optimal conditions employing a Cu-I triflate complex (10 mol%) in dichloroethane-MeCN and mol. sieves with air as the oxidant, aryl coupling of naphthol derivs. could be achieved in satisfactory yields (48-90% yield) and ees of up to 65%. The ester moiety at the 3-position of the substrate was found to be crucial for a satisfactory asym. induction in the present coupling reaction.

- ST diamine camphor copper catalyst oxidative coupling naphthol
- Phenols, reactions

RL: RCT (Reactant); RACT (Reactant or reagent)

(naphthols; preparation of bis[trimethylbicycloheptyl]ethanediamine as ligand for oxidative biaryl coupling of naphthol derivs. with copper catalyst)

(of bis[trimethylbicycloheptyl]ethanediamine as ligand for oxidative biaryl coupling of naphthol derivs. with copper catalyst)

IT Coupling reaction catalysts

> (oxidative; preparation of bis[trimethylbicycloheptyl]ethanediamine as ligand for oxidative biaryl coupling of naphthol derivs. with copper catalyst)

IT 592544-50-8P

> RL: PRP (Properties); SPN (Synthetic preparation); PREP (Preparation) (crystal structure; preparation of bis[trimethylbicycloheptyl]ethanediamine as ligand for oxidative biaryl coupling of naphthol derivs. with copper catalyst)

TT 187989-61-3P

> RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent) (preparation and reduction of)

592544-48-4P

RL: CAT (Catalyst use); RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent); USES (Uses)

(preparation as ligand for oxidative biaryl coupling of naphthol derivs. with copper catalyst)

IT 180857-93-6

RL: CAT (Catalyst use); USES (Uses)

(preparation of bis[trimethylbicycloheptyl]ethanediamine as ligand for oxidative biaryl coupling of naphthol derivs. with copper catalyst)

135-19-3, 2-Naphthol, reactions 883-99-8 17056-93-8 IT 98793-02-3 127363-96-6

RL: RCT (Reactant); RACT (Reactant or reagent)

(preparation of bis[trimethylbicycloheptyl]ethanediamine as ligand for oxidative biaryl coupling of naphthol derivs. with copper catalyst)

502 naphthol 55515-98-5P 592544-49-5P 595567 etic pro 3515-98-5P 145415-62-9P 595561-28-7P 18531-94-7P 18531-91-4P 223903-32-0P 342630-36-8P

RL: SPN (Synthetic preparation); PREP (Preparation)

(preparation of bis[trimethylbicycloheptyl]ethanediamine as ligand for oxidative biaryl coupling of naphthol derivs. with copper catalyst)

107-15-3, Ethylenediamine, reactions IT

RL: RCT (Reactant); RACT (Reactant or reagent) (reaction with camphor)

464-49-3, (1R)-(+)-Camphor

RL: RCT (Reactant); RACT (Reactant or reagent) (reaction with ethylenediamine)

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- (14) Periasamy, M; Synth Commun 1989, V19, P565 HCAPLUS
- (15) Raza, Z; Croat Chem Acta 1996, V69, P1545 HCAPLUS
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- (17) Sheldrick, G; SHELX-97 Program for the Refinement of Crystal Structures 1997

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(18) Smrcina, M; J Org Chem 1993, V58, P4534 HCAPLUS
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- IT 187989-61-3P

RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)

(preparation and reduction of)

- RN 187989-61-3 HCAPLUS
- CN 1,2-Ethanediamine, N,N'-bis[(1R,4R)-1,7,7-trimethylbicyclo[2.2.1]hept-2-ylidene]-, (E,E)- (9CI) (CA INDEX NAME)

Absolute stereochemistry.

Double bond geometry as shown.

- L49 ANSWER 2 OF 27 HCAPLUS COPYRIGHT 2004 ACS on STN
- AN 2001:547138 HCAPLUS
- DN 135:303448
- ED Entered STN: 29 Jul 2001
- TI Tetraethylammonium bromide catalyzed phase transfer reaction of potassium superoxide with hydrazones and tosylhydrazones
- AU Kumar, Rajesh; Singh, Krishna Nand
- CS Department of Applied Chemistry, Institute of Technology, Banaras Hindu University Varanasi 221005 India
- University, Varanasi, 221005, India
  SO Indian Journal of Chemistry, Section B: Organic Chemistry Including
  Medicinal Chemistry (2001), 40B(7), 579-583
  CODEN: IJSBDB; ISSN: 0376-4699
- PB National Institute of Science Communication
- DT Journal
- LA English
- CC 21-2 (General Organic Chemistry)
- OS CASREACT 135:303448
- AB A variety of hydrazones and tosylhydrazones of carbonyl compds. have been investigated under the mild reaction conditions of potassium superoxide and tetraethylammonium bromide in dry DMF. As a result, hydrazones are generally transformed into azines whereas tosylhydrazones undergo facile fragmentation to give olefinic products in fairly good yields. The study highlights the use of tetraethylammonium bromide as an efficient and inexpensive catalyst for superoxide studies.
- ST tetraethylammonium bromide catalyst superoxide reaction hydrazone tosylhydrazone; azine prepn tetraethylammonium bromide catalyst; olefin prepn tetraethylammonium bromide catalyst; phase transfer superoxide reaction hydrazone tosylhydrazone
- IT Phase transfer catalysts

(oxidation; tetraethylammonium bromide catalyzed phase transfer reaction of potassium superoxide with hydrazones and tosylhydrazones)

IT Oxidation catalysts

(phase transfer; tetraethylammonium bromide catalyzed phase transfer reaction of potassium superoxide with hydrazones and tosylhydrazones)

(phase-transfer; tetraethylammonium bromide catalyzed phase transfer reaction of potassium superoxide with hydrazones and tosylhydrazones) Hydrazones

RL: RCT (Reactant); RACT (Reactant or reagent)

(tetraethylammonium bromide catalyzed phase transfer reaction of potassium superoxide with hydrazones and tosylhydrazones)

IT Alkenes, preparation

RL: SPN (Synthetic preparation); PREP (Preparation)

(tetraethylammonium bromide catalyzed phase transfer reaction of potassium superoxide with hydrazones and tosylhydrazones)

IT Azines

IT

IT

RL: SPN (Synthetic preparation); PREP (Preparation)

(tetraethylammonium bromide catalyzed phase transfer reaction of potassium superoxide with hydrazones and tosylhydrazones)

Kumar 10/612609

Page 13

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IT
      Cycloalkenes
      RL: SPN (Synthetic preparation); PREP (Preparation)
          (tetraethylammonium bromide catalyzed phase transfer reaction of
          potassium superoxide with hydrazones and tosylhydrazones)
      71-91-0, Tetraethylammonium bromide
      RL: CAT (Catalyst use); RCT (Reactant); RACT (Reactant or reagent); USES
      (Uses)
          (tetraethylammonium bromide catalyzed phase transfer reaction of
         potassium superoxide with hydrazones and tosylhydrazones)
      770-53-6, Camphor hydrazone 1666-17-7, Benzaldehyde tosylhydrazone
      4545-18-0, Cyclohexanone tosylhydrazone
                                                         4545-20-4, Benzophenone
     tosylhydrazone 5344-88-7, Benzil monohydrazone 5350-57-2, Benzophenone hydrazone 5463-11-6, 4,4'-Dichlorobenzophenone hydrazone 12030-88-5, Potassium superoxide 13466-30-3, Acetophenone hydrazone 13629-22-6,
      Fluoren-9-one hydrazone 18708-16-2 19350-72-2, 4-Methoxybenzaldehyde tosylhydrazone 20114-55-0, 4,4'-Dimethoxybenzophenone hydrazone 52826-41-2 65111-92-4, 4,4'-Bis(dimethylamino)benzophenone hydrazone
      68384-27-0
      RL: RCT (Reactant); RACT (Reactant or reagent)
          (tetraethylammonium bromide catalyzed phase transfer reaction of
          potassium superoxide with hydrazones and tosylhydrazones)
IT
      54260-53-6P, Tetraethylammonium superoxide
      RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT
      (Reactant or reagent)
          (tetraethylammonium bromide catalyzed phase transfer reaction of
          potassium superoxide with hydrazones and tosylhydrazones)
      103-30-0P, trans-Stilbene 110-83-8P, Cyclohexene, preparation
IT
      451-40-1P, 2-Phenylacetophenone 591-49-1P, 1-Methylcyclohexene 632-51-9P, Tetraphenylethylene 983-79-9P, Benzophenone azine 1931-49-3P, 4,4'-
      Bis(dimethylamino)stilbene 2071-44-5P, Fluoren-9-one azine 4705-3-4,4'-Dimethoxystilbene 5831-42-5P, 4,4'-Dimethoxybenzophenone azine
                                                                                    4705-34-4P.
      47180-21-2P, Camphor azine 50482-89-8P 82907-50-4P
      RL: SPN (Synthetic preparation); PREP (Preparation)
          (tetraethylammonium bromide catalyzed phase transfer reaction of
          potassium superoxide with hydrazones and tosylhydrazones)
                 THERE ARE 35 CITED REFERENCES AVAILABLE FOR THIS RECORD
RE.CNT
RE

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47180-21-2P, Camphor azine
     RL: SPN (Synthetic preparation); PREP (Preparation)
        (tetraethylammonium bromide catalyzed phase transfer reaction of
        potassium superoxide with hydrazones and tosylhydrazones)
RN
     47180-21-2 HCAPLUS
     Bicyclo[2.2.1]heptan-2-one, 1,7,7-trimethyl-, (1,7,7-
     trimethylbicyclo[2.2.1]hept-2-ylidene)hydrazone (9CI) (CA INDEX NAME)
      Me
    ANSWER 3 OF 27 HCAPLUS COPYRIGHT 2004 ACS on STN
     2001:340740 HCAPLUS
AN
     135:122006
DN
ED
     Entered STN: 14 May 2001
     A convenient synthesis of azines under solvent-free conditions using
TI
     microwave irradiation
     Loghmani-Khouzani, Hossein; Sadeghi, Majid M. M.; Safari, Javad;
AU
     Abdorrezaie, Mohammad S.; Jafarpisheh, Masood
CS
     Department of Chemistry, Faculity of Sciences, University of Isfahan,
     Esfahan, 81744, Iran
     Journal of Chemical Research, Synopses (2001), (2), 80-81
SO
     CODEN: JRPSDC; ISSN: 0308-2342
PB
     Science Reviews Ltd.
DT
     Journal
LΑ
     English
CC
     21-2 (General Organic Chemistry)
     CASREACT 135:122006
os
     In an extremely fast method the reaction of hydrazine sulfate with a number
AB
     of aldehydes and ketones is accelerated by microwave irradiation under
     solvent-free conditions in the presence of CH3CO2Na/CaCl2 to afford high
     yields of azines.
     azine prepn microwave; hydrazine sulfate condensation aldehyde ketone
ST
     microwave
IT
     Condensation reaction
     Microwave
        (azine preparation under solvent-free conditions using microwave irradiation)
IT
     Aldehydes, reactions
     Ketones, reactions
     RL: RCT (Reactant); RACT (Reactant or reagent)
        (azine preparation under solvent-free conditions using microwave irradiation)
IT
     Azines
     RL: SPN (Synthetic preparation); PREP (Preparation)
        (azine preparation under solvent-free conditions using microwave irradiation)
     76-22-2, Camphor 90-02-8, 2-Hydroxybenzaldehyde, reactions 98-86-2,
     Acetophenone, reactions
                              99-61-6, 3-Nitrobenzaldehyde 100-10-7,
     4-(Dimethylamino)benzaldehyde 100-52-7, Benzaldehyde, reactions
     104-55-2, Cinnamaldehyde 108-94-1, Cyclohexanone, reactions
                                                                     119-53-9,
               119-61-9, Benzophenone, reactions
                                                   123-11-5,
     4-Methoxybenzaldehyde, reactions 127-09-3, Sodium acetate 134-81-6,
                                               10034-93-2, Hydrazine sulfate
             1531-38-0, 2-Phenacylquinoline
     Benzil
     10043-52-4, Calcium chloride, reactions
                                               83319-24-8
     RL: RCT (Reactant); RACT (Reactant or reagent)
        (azine preparation under solvent-free conditions using microwave irradiation)
     588-68-1P, Benzaldehyde azine 729-43-1P, Acetophenone azine 959-36-4P,
     Salicylaldehyde azine 983-79-9P, Benzophenone azine 156
1568-11-2P, Cinnamaldehyde azine 2143-98-8P 2299-73-2P,
                                                             1567-91-5P
     4-Methoxybenzaldehyde azine 3893-33-2P, Benzil azine 4278-87-9P,
     Cyclohexanone azine 47180-21-2P, Camphor azine
                                                     124951-88-8P
     351183-99-8P
                   351184-00-4P
     RL: SPN (Synthetic preparation); PREP (Preparation)
        (azine preparation under solvent-free conditions using microwave irradiation)
RE.CNT 13
              THERE ARE 13 CITED REFERENCES AVAILABLE FOR THIS RECORD
RE
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trimethylbicyclo[2.2.1]hept-2-ylidene)hydrazone (9CI) (CA INDEX NAME)

ANSWER 4 OF 27 HCAPLUS COPYRIGHT 2004 ACS on STN

Complexes of the (1R)-(+)-camphor azine diphosphines Z,Z-3,3'-

Ph2PnC10H15=N-N=C10H15PxPh2 and Z,Z-3,3'-Ph2PxC10H15=N-N=C10H15PxPh2 (x =

129:144165

1998:393621 HCAPLUS

Entered STN: 27 Jun 1998

L49

AN

ED

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exo, n = endo) with Group 6 metal carbonyls: crystal structures of the
     ligands and fac-[W(CO)3(E,Z-Ph2PxC10H15=N-N=C10H15PxPh2)]
     Shaw, Bernard L.; Iranpoor, Nasser; Perera, Sarath D.; Thornton-Pett,
AU
     Mark; Vessey, Jonathan D.
CS
     Sch. Chem., Univ. Leeds, Leeds, LS2 9JT, UK
     Journal of the Chemical Society, Dalton Transactions: Inorganic Chemistry
     (1998), (11), 1885-1891
CODEN: JCDTBI; ISSN: 0300-9246
PB
     Royal Society of Chemistry
     Journal
DT
LΑ
     English
     78-7 (Inorganic Chemicals and Reactions)
CC
     Section cross-reference(s): 29, 75
     Treatment of (1R)-(+)-camphor azine with 2 mol equivalent of butyllithium,
AB
     followed by chlorodiphenylphosphine, gave the azine diphosphines Z,Z-3,3'-Ph2PxC10H15:N-N:C10H15PxPh2 (I) and Z,Z-3,3'-Ph2PxC10H15:N-
     N:Cl0H15PxPh2 (II) (x = exo, n = endo); the structures of I and
     II.cntdot.3CHCl3 were determined by x-ray diffraction. On boiling an ethanol solution of the exo,exo-diphosphine II with sodium ethoxide or a propan-2-ol
      solution containing hydrazine hydrate and acetic acid the diphosphine isomerized
      to the corresponding exo, endo-diphosphine I. The corresponding
     diphosphine dioxides (III and IV) were prepared by treating I or II with
     H2O2, resp. Treatment of I with [Mo(CO)4(nbd)] (nbd = norbornadiene) or
      with [Mo(CO)3(cht)] (cht = cyclohepta-1,3,5-triene) gave
      fac-[Mo(CO)3(Ph2PnC10H15:N-N:C10H15PxPh2)] (la). Treatment of I with
      [W(CO)4(nbd)] gave the tricarbonyltungsten(0) complex fac-
      [W(CO)3(Ph2PnC10H15:N-N:C10H15PxPh2)] (1b) and the analogous mer complex
      mer-[W(CO)3(Ph2PnC10H15:N-N:C10H15PxPh2)] (2). Treatment of II with
      [W(CO)6] gave the mer, exo, endo tricarbonyl complex 2, and the
      fac, endo, endo complex fac-[W(CO)3(Ph2PnC10H15:N-N:C10H15PnPh2)] (3).
     Treatment of II with [M(CO) 4 (nbd)] (M = Mo, W or Cr) gave mainly fac-[M(CO) 3 (Ph2PxC10H15:N-N:C10H15PxPh2)] (M = Mo 4a, W 4b or Cr 4c).
      crystal structure of the tricarbonyltungsten(0) complex 4b.cntdot.EtOH was
     determined by x-ray diffraction and the chirality around tungsten shown to be
     C, i.e. clockwise. Treatment of 4b with 1 mol equivalent of bromine gave the
     tricarbonyltungsten(II) bromide salt [WBr(CO)3(Ph2PxCl0H15:N-N:Cl0H15PxPh2)]Br (5). IR, proton, phosphorus-31 and some carbon-13 NMR
      data are given.
     camphor azine diphosphine prepn isomerization complexation; transition
     metal camphor azine diphosphine prepn; tungsten camphor azine diphosphine
      prepn structure; molybdenum camphor azine diphosphine complex prepn;
      chromium camphor azine diphosphine complex prepn; crystal structure
      tungsten camphor azine diphosphine
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IT
     Isomerization
         (endo-exo; of camphor azine diphosphine)
IT
     Crystal structure
     Molecular structure
         (of camphor azine diphosphine and its tungsten complex)
     Transition metal complexes
     RL: SPN (Synthetic preparation); PREP (Preparation)
         (preparation of transition metal camphor azine diphosphine complexes)
     1079-66-9, Chlorodiphenylphosphine
                                              173396-18-4
IT
     RL: RCT (Reactant); RACT (Reactant or reagent)
         (for preparation of camphor azine diphosphine isomers and their oxides and
         transition metal complexes)
     12125-77-8, Tricarbonyl (cyclohepta-1,3,5-triene) molybdenum
Tetracarbonyl (norbornadiene) tungsten 12146-36-0,
                                                                         12129-25-8.
IT
     Tetracarbonyl (norbornadiene) chromium
                                                12146-37-1,
     Tetracarbonyl (norbornadiene) molybdenum 14040-11-0, Tungsten hexacarbonyl
     RL: RCT (Reactant); RACT (Reactant or reagent)
         (for preparation of transition metal camphor azine diphosphine complex)
     210530-92-0P 210647-79-3P
     RL: PRP (Properties); SPN (Synthetic preparation); PREP (Preparation)
         (preparation and crystal structure)
     210588-63-9P
TT
     RL: PRP (Properties); SPN (Synthetic preparation); PREP (Preparation)
         (preparation and mol. structure)
     210530-80-6P 210530-81-7P 210530-82-8P 210530-83-9P 210530-87-3P 210530-90-8P 210588-60-6P 210588-61-7P
                                                                         210588-62-8P
     RL: SPN (Synthetic preparation); PREP (Preparation)
         (preparation of)
IT
     210530-78-2P
     RL: PRP (Properties); RCT (Reactant); SPN (Synthetic preparation); PREP
     (Preparation); RACT (Reactant or reagent)
         (preparation, crystal structure, oxidation to phosphine oxide and complexation
         with molybdenum and tungsten)
IT
     210530-79-3P
     RL: PRP (Properties); RCT (Reactant); SPN (Synthetic preparation); PREP
      (Preparation); RACT (Reactant or reagent)
         (preparation, mol. structure, endo-exo isomerization, oxidation to phosphine
         oxide and complexation with transition metals)
RE.CNT
               THERE ARE 28 CITED REFERENCES AVAILABLE FOR THIS RECORD
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(28) Walter, N; Acta Crystallogr, Sect A 1983, V39, P158
     210530-92-0P
TΤ
     RL: PRP (Properties); SPN (Synthetic preparation); PREP (Preparation)
         (preparation and crystal structure)
     210530-92-0 HCAPLUS
     Bicyclo[2.2.1]heptan-2-one, 3-(diphenylphosphino)-1,7,7-trimethyl-
      (2Z) - [(1R,3R,4S)-3-(diphenylphosphino)-1,7,7-trimethylbicyclo[2.2.1]hept-2-
     ylidene]hydrazone, (1R,2Z,3R,4S)-, compd. with trichloromethane (1:3)
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(9CI) (CA INDEX NAME)

CM

CRN 210530-79-3 CMF C44 H50 N2 P2

Absolute stereochemistry. Double bond geometry as shown.

CM

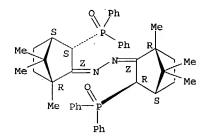
CRN 67-66-3 CMF C H Cl3

IT 210530-80-6P 210530-81-7P RL: SPN (Synthetic preparation); PREP (Preparation) (preparation of)

RN

210530-80-6 HCAPLUS
Bicyclo[2.2.1]heptan-2-one, 3-(diphenylphosphinyl)-1,7,7-trimethyl-, CN (2Z) - [(1R, 3R, 4S) -3 - (diphenylphosphinyl) -1, 7, 7-trimethylbicyclo[2.2.1]hept-2-ylidene]hydrazone, (1R,2Z,3S,4S)- (9CI) (CA INDEX NAME)

Absolute stereochemistry. Double bond geometry as shown.



RN210530-81-7 HCAPLUS

Bicyclo[2.2.1]heptan-2-one, 3-(diphenylphosphinyl)-1,7,7-trimethyl-, (2Z)-[(1R,3R,4S)-3-(diphenylphosphinyl)-1,7,7-trimethylbicyclo[2.2.1]hept-2-ylidene]hydrazone, (1R,2Z,3R,4S)- (9CI) (CA INDEX NAME) CN

Absolute stereochemistry. Double bond geometry as shown.

IT 210530-78-2P
 RL: PRP (Properties); RCT (Reactant); SPN (Synthetic preparation); PREP
 (Preparation); RACT (Reactant or reagent)
 (preparation, crystal structure, oxidation to phosphine oxide and complexation
 with molybdenum and tungsten)
RN 210530-78-2 HCAPLUS
CN Bicyclo{2.2.1}heptan-2-one, 3-(diphenylphosphino)-1,7,7-trimethyl-,
 (22)-[(1R,3R,4S)-3-(diphenylphosphino)-1,7,7-trimethylbicyclo[2.2.1]hept-2 ylidene]hydrazone, (1R,2Z,3S,4S)- (9CI) (CA INDEX NAME)

Absolute stereochemistry.

Double bond geometry as shown.

IT 210530-79-3P

RL: PRP (Properties); RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)

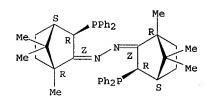
(preparation, mol. structure, endo-exo isomerization, oxidation to phosphine oxide and complexation with transition metals)

RN 210530-79-3 HCAPLUS

CN Bicyclo[2.2.1]heptan-2-one, 3-(diphenylphosphino)-1,7,7-trimethyl-, (2Z)-[(1R,3R,4S)-3-(diphenylphosphino)-1,7,7-trimethylbicyclo[2.2.1]hept-2-ylidene]hydrazone, (1R,2Z,3R,4S)- (9CI) (CA INDEX NAME)

Absolute stereochemistry.

Double bond geometry as shown.



- L49 ANSWER 5 OF 27 HCAPLUS COPYRIGHT 2004 ACS on STN
- AN 1997:462096 HCAPLUS
- DN 127:212365
- ED Entered STN: 24 Jul 1997
- TI Photoinitiated rearrangements of 3-phenylnorbornadiene with conjugated substituents in 2-position
- AU Chernoivanov, Vladimir A.; Dubonosov, Alexander D.; Bren, Vladimir A.; Minkin, Vladimir I.; Suslov, Alexander N.; Borodkin, Gennadii S.
- CS Institute Physical Organic Chemistry, Rostov State University, Rostov on Don, 344090, Russia
- SO Molecular Crystals and Liquid Crystals Science and Technology, Section A: Molecular Crystals and Liquid Crystals (1997), 297, 239-245
  CODEN: MCLCE9; ISSN: 1058-725X
- PB Gordon & Breach
- DT Journal
- LA English
- CC 74-1 (Radiation Chemistry, Photochemistry, and Photographic and Other Reprographic Processes) .
  Section cross-reference(s): 22, 52
- As eries of novel 3-phenylnorbornadienes with conjugated substituents in 2-position (carbaldimine, carbaldoxime, amide, aroylvinyl and heterocyclic groups) have been synthesized. All the compds. obtained absorb in the 310-420 nm spectral region and under UV-Vis-irradiation form corresponding quadricyclanes with quantum yields in the range of 0.1-0.7. The back reaction proceeds almost quant. yield under homogeneous and heterogeneous catalysis or on heating.
- ST photorearrangement phenylnorbornadiene photolysis photoisomerization photochromism spectra

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IT
     Photochromism
     Photolysis
     UV and visible spectra
        (photoinitiated rearrangements of 3-phenylnorbornadiene with conjugated
        substituents in 2-position)
IT
     Isomerization
        (photoisomerization; photoinitiated rearrangements of
        3-phenylnorbornadiene with conjugated substituents in 2-position)
                  158197-96-7
IT
     147678-07-7
                                 158197-97-8
                                               158197-98-9
                                                              158197-99-0
                   158198-01-7
     158198-00-6
                                 158198-02-8 158198-03-9
     158815-83-9
                   158815-84-0
                                 158815-85-1
                                               158815-86-2
                                                              160346-44-1
     160346-50-9
                   176100-81-5
                                 194658-32-7
                                               194658-33-8
                                                              194658-34-9
     194658-35-0
                   194658-36-1
                                 194658-37-2
                                               194658-38-3
                                                              194658-39-4
     194658-40-7
                  194658-41-8
     RL: FMU (Formation, unclassified); PRP (Properties); FORM (Formation,
     nonpreparative)
        (photoinitiated rearrangements of 3-phenylnorbornadiene with conjugated
        substituents in 2-position)
     123316-35-8
                  123316-36-9
                                 147678-04-4
                                               158197-86-5
                                                              158197-87-6
     158197-88-7
                   158197-89-8
                                 158197-90-1
                                               158197-91-2
                                                              158197-92-3
     158197-93-4
                   158197-94-5
                                 158815-79-3
                                               158815-80-6
                                                              158815-81-7
     158815-82-8
                   160346-42-9
                                 176100-80-4
                                               194658-16-7
                                                              194658-17-8
     194658-20-3
                   194658-21-4
                                 194658-22-5
                                               194658-23-6
                                                              194658-24-7
     194658-25-8
                   194658-26-9
                                 194658-28-1
                                               194658-29-2
                                                              194658-30-5
     194658-31-6
     RL: PRP (Properties); RCT (Reactant); RACT (Reactant or reagent)
        (photoinitiated rearrangements of 3-phenylnorbornadiene with conjugated
        substituents in 2-position)
IT
     158198-03-9
     RL: FMU (Formation, unclassified); PRP (Properties); FORM (Formation,
     nonpreparative)
        (photoinitiated rearrangements of 3-phenylnorbornadiene with conjugated
        substituents in 2-position)
RN
     158198-03-9 HCAPLUS
     Tetracyclo[3.2.0.02,7.04,6]heptane-1-carboxamide, N-2-naphthalenyl-5-
```

phenyl- (9CI) (CA INDEX NAME)

```
ANSWER 6 OF 27 HCAPLUS COPYRIGHT 2004 ACS on STN
AN
     1997:106714 HCAPLUS
DN
     126:212258
ED
     Entered STN: 14 Feb 1997
     Structural properties of some C2-symmetric Schiff bases and
TI
     stereoselectivity in cyclopropanation of styrene by their Cu(I) complexes
ΑU
     Raza, Zlata; Dakovic, Senka; Vinkovic, Vladimir; Sunjic, Vitomir
CS
     Ruder Boskovic Institute, Zagreb, 10000, Croatia
     Croatica Chemica Acta (1996), 69(4), 1545-1559
so
     CODEN: CCACAA; ISSN: 0011-1643
PB
     Croatian Chemical Society
\mathbf{DT}
LА
     English
     30-10 (Terpenes and Terpenoids)
CC
     Section cross-reference(s): 22
os
     CASREACT 126:212258
GI
```

AB C2-sym. Schiff bases derived from R-camphor and R-fenchone were prepared, their configurational and conformational features determined by 1D- and 2D-NMR spectra and supported by MM2 calcns. Their Cu(I) complexes prepared in situ were examined in cyclopropanation of styrene and low to medium e.e.'s (2-32%) were obtained. Correlation of the structure of E,E-I and Z,Z-II with enantioselectivity of their Cu(I) complexes revealed restricting steric requirements in the former, possessing gem di-Me group in the proximity of the chiral center, near to the coordination sphere of alkene and carbene, as the probable origin of its higher enantioselectivity. Schiff base camphor fenchone prepn; conformation Schiff base camphor fenchone; cyclopropanation catalyst camphor fenchone Schiff base; copper camphor fenchone Schiff base

IT Cyclopropanation

(stereoselective; structural properties of C2-sym. Schiff bases and stereoselectivity in cyclopropanation of styrene by Cu(I) complexes)

TT Asymmetric synthesis and induction

Conformation

Cyclopropanation catalysts

Molecular mechanics

(structural properties of C2-sym. Schiff bases and stereoselectivity in cyclopropanation of styrene by Cu(I) complexes)

IT 42152-44-3, Cuprous trifluoromethanesulfonate

RL: CAT (Catalyst use); USES (Uses)

(structural properties of C2-sym. Schiff bases and stereoselectivity in cyclopropanation of styrene by Cu(I) complexes)

TΤ 187989-61-3P 187989-62-4P 187989-63-5P

187989-64-6P 187989-65-7P 187989-66-8P

RL: CAT (Catalyst use); PRP (Properties); SPN (Synthetic preparation); PREP (Preparation); USES (Uses)

(structural properties of C2-sym. Schiff bases and stereoselectivity in cyclopropanation of styrene by Cu(I) complexes)

95-54-5, o-Phenylenediamine, reactions 100-42-5, Styrene, reactions 107-15-3, 1,2-Ethanediamine, reactions 108-45-2, m-Phenylenediamine, reactions 109-76-2, 1,3-Propanediamine 110-60-1, 1,4-Butanediamine 464-49-3, R-Camphor 623-73-4, Ethyl diazoacetate 7787-20-4,

(-)-Fenchone 63254-50-2 65437-23-2 RL: RCT (Reactant); RACT (Reactant or reagent)

(structural properties of C2-sym. Schiff bases and stereoselectivity in cyclopropanation of styrene by Cu(I) complexes)

34702-97-1P 34716-60-4P ( 120143-38-6P 120143-39-7P 34702-96-0P 67489-30-9P 67528-67-0P

105367-38-2P

RL: SPN (Synthetic preparation); PREP (Preparation)

(structural properties of C2-sym. Schiff bases and stereoselectivity in cyclopropanation of styrene by Cu(I) complexes)

RE.CNT 27 THERE ARE 27 CITED REFERENCES AVAILABLE FOR THIS RECORD RE

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- (4) Cudic, P; Tetrahedron 1991, V47, P5295 HCAPLUS
- (5) Evans, D; J Am Chem Soc 1991, V113, P726 HCAPLUS
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- (17) Lautenegger, U; Tetrahedron 1992, V48, P2143
- (18) Li, Z; J Am Chem Soc 1993, V115, P5326 HCAPLUS
- (19) Loewenthal, R; Tetrahedron Lett 1990, V31, P6005 (20) Loewenthal, R; Tetrahedron Lett 1991, V32, P7373
- (21) Moberg, C; Acta Chem Scand 1996, V59, P195
- (22) Muller, D; Helv Chim Acta 1991, V74, P232 (23) Nishiyama, H; Organometallics 1991, V10, P500 HCAPLUS
- (24) Raza, Z; Croat Chem Acta 1991, V64, P65 HCAPLUS
- (25) Sunjic, V; Tetrahedron: Asymmetry 1993, V4, P575 HCAPLUS
- (26) Von Matt, P; Tetrahedron: Asymmetry 1991, V2, P691 HCAPLUS
- (27) Zhang, W; J Am Chem Soc 1990, V112, P2801 HCAPLUS
- 187989-61-3P 187989-62-4P 187989-63-5P

RL: CAT (Catalyst use); PRP (Properties); SPN (Synthetic preparation);

PREP (Preparation); USES (Uses)

(structural properties of C2-sym. Schiff bases and stereoselectivity in cyclopropanation of styrene by Cu(I) complexes)

RN 187989-61-3 HCAPLUS

 $\label{eq:continuous} 1, 2\text{-Ethanediamine, N,N'-bis} \ [\ (1R,4R)-1,7,7-\text{trimethylbicyclo} \ [2.2.1] \ \text{hept-2-like} \ ]$ CN ylidene]-, (E,E)- (9CI) (CA INDEX NAME)

Absolute stereochemistry. Double bond geometry as shown.

$$\begin{array}{c} \text{Me} \\ \text{Me} \\$$

187989-62-4 HCAPLUS

1,3-Propanediamine, N,N'-bis(1,7,7-trimethylbicyclo[2.2.1]hept-2-ylidene)-CN , [1R-[1.alpha.,2E[E(1R\*,4R\*)],4.alpha.]]- (9CI) (CA INDEX NAME)

Absolute stereochemistry. Double bond geometry as shown.

$$\begin{array}{c} \text{Me} \\ \text{R} \\ \text{Me} \\ \text{R} \end{array}$$

187989-63-5 HCAPLUS RN

CN 1,4-Butanediamine, N,N'-bis(1,7,7-trimethylbicyclo[2.2.1]hept-2-ylidene)-, [1R-[1.alpha.,2E[E(1R\*,4R\*)],4.alpha.]]- (9CI) (CA INDEX NAME)

Absolute stereochemistry. Double bond geometry as shown.

Kumar 10/612609 Page 22

ANSWER 7 OF 27 HCAPLUS COPYRIGHT 2004 ACS on STN L49 1995:984317 HCAPLUS AN 124:163141 DN Entered STN: 14 Dec 1995 ED A general method of generating agostic interaction between RuII and C-H TT bonds of tert-butyl, methyl, aryl, heterocyclic or alkenyl groups using azine phosphines AU Perera, Sarath D.; Shaw, Bernard L. School of Chemistry, University of Leeds, Leeds, LS2 9JT, UK CS Journal of the Chemical Society, Dalton Transactions: Inorganic Chemistry SO (1995), (23), 3861-66 CODEN: JCDTBI; ISSN: 0300-9246 Royal Society of Chemistry PBJournal DТ LA English 78-7 (Inorganic Chemicals and Reactions) CC Treatment of [RuCl2(PPh3)3] (2) with the azine phosphine Z,E-PPh2CH2C(But)=N-N=C(Me)But 3a, derived from MeC(=0)But, gave the .delta.-agostic tert-Bu complex mer,trans-[RuCl2(PPh3){PPh2CH2-C(But)=N-N=C(Me)But ]] (4a), in which all nine hydrogens of the tert-Bu group are agostically interacting with Ru on the NMR time-scale at 20.degree. The analogous .delta.-agostic tert-Bu complex mer, trans-[RuCl2(PPh3){PPh2CH2C(But)=N-N-C(H)But}] (4b) was also prepared Treatment of 2 with the sym. azine diphosphine Z,Z-PPh2CH2C(But)=N-N-C(But)CH2PPh2 (5) gave the .delta.-agostic tert-Bu complex mer, trans-[RuCl2(PPh3){PPh2CH2C(But)=N-N=C(But)CH2PPh2}] (6), in which one of the PPh2 groups is uncoordinated. Treatment of 2 with the azine phosphine Z,E-PPh2CH2C(But)=N-N=C10H16 (7), derived from pinacolone-fenchone mixed azine, gave the .delta.-agostic Me complex mer, trans-[RuCl2(PPh3){PPh2CH2C(But)=N-N=C10H16}] (8), in which the Me group (C10H3) in the 1-position of the fenchone residue interacts with Ru (fenchone = 1,3,3-trimethylbicyclo[2.2.1]heptan-2-one). The unsym. camphor azine monophosphine Z,Z-PPh2-C10H15=N-N=C10H16 (9) also gave a similar .delta.-agostic Me complex mer,trans-[RuCl2(PPh3){PPh2-C10H15=N-N=C10H16}] (10) (camphor = 1,7,7-trimethylbicyclo[2.2.1]heptan-2-one). Treatment of 2 with the azine Z,E-PPh2CH2C(But)=N-N=CH(C6H4NMe2-4) lla, derived from 4-dimethylaminobenzaldehyde, gave the .delta.-agostic complex mer, trans-[RuCl2(PPh3){PPh2CH2C(But)=N-N=CH(C6H4NMe2-4)}] (12a), in which the hydrogens in the 2- and 6-positions of the aryl group are agostically interacting with Ru. Similarly, the azines 11b and 11c, derived from 4-methoxybenzaldehyde or 4-mitrobenzaldehyde, gave the .delta.-agostic complexes 12b and 12c, resp. Treatment of 2 with the azine 13, derived from 1-methylpyrrole-2-carbaldehyde, gave the .delta.-agostic complex 14, in which the H in the 3-position of the heterocyclic group is agostically interacting with Ru. Treatment of 2 with the azine 15, derived from benzylideneacetone, gave the .delta.-agostic alkenyl complex 16. Proton, 31P-{1H} and some 13C-{1H} NMR data are given. ruthenium azine phosphine prepn agostic bond RL: PRP (Properties); SPN (Synthetic preparation); PREP (Preparation) (ruthernium chloro phosphine azine complexes; preparation and agostic bonds in) IT (agostic, in ruthenium azine phosphine complexes) 108-18-9, Diisopropylamine 1079-66-9, Chlorodiphenylphosphine IT 173396-18-4, (1R)-(+)-Camphor azine RL: RCT (Reactant); RACT (Reactant or reagent) (for preparation of azine phosphine and its ruthenium complex with agostic bond) 158273-99-5P 158274-00-1P 158274-01-2P 158274-02-3P 158308-33-9P 173283-23-3P 173283-24-4P 173283-25-5P 173283-26-6P 173283-22-2P RL: PRP (Properties); SPN (Synthetic preparation); PREP (Preparation) (preparation and agostic bonding in) 156783-26-5P 156783-27-6P 173283-21-1P 156783-25-4P RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent) (preparation and reaction with ruthenium chloro triphenylphosphine complex) 155606-61-4 156783-24-3 157064-00-1 IT 143627-09-2 157064-07-8 RL: RCT (Reactant); RACT (Reactant or reagent) (reaction with ruthenium chloro triphenylphosphine complex) 15529-49-4, Dichlorotris (triphenylphosphine) ruthenium TT RL: RCT (Reactant); RACT (Reactant or reagent) (reactions with azine phosphines for preparation of azine chloro complexes with agostic bonds)

TT

156783-25-4P

Kumar 10/612609

Page 23

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RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT
     (Reactant or reagent)
        (preparation and reaction with ruthenium chloro triphenylphosphine complex)
RN
     156783-25-4 HCAPLUS
CN
     Bicyclo[2.2.1]heptan-2-one, 3-(diphenylphosphino)-1,7,7-trimethyl-,
     (1,7,7-trimethylbicyclo[2.2.1]hept-2-ylidene)hydrazone,
     [1S-[1.alpha.,2(1R*,4R*),3.beta.,4.alpha.]]- (9CI) (CA INDEX NAME)
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L49

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ANSWER 8 OF 27 HCAPLUS COPYRIGHT 2004 ACS on STN
     1995:437526 HCAPLUS
AN
DN
     122:314842
ED
     Entered STN: 23 Mar 1995
ТI
     Studies on the asymmetric oxidative coupling reaction of (+)-camphor imine
     carbanions
     Liu, Gui-Lan; Hu, Wen-Hao; Ma, Yu-Zhi; Jiang, Yao-Zhong
AU
     Chengdu Inst. Org. Chem., Chinese Academy Sci., Chengdu, 610041, Peop.
CS
     Rep. China
so
     Huaxue Xuebao (1995), 53(2), 183-7
     CODEN: HHHPA4; ISSN: 0567-7351
PB
     Kexue
DT
     Journal
LΑ
     Chinese
CC
     30-10 (Terpenes and Terpenoids)
     Section cross-reference(s): 22
AB
     The paper studies on asym. coupling reaction of (+)-camphor imine
     carbanions. The ratio of threo to erythro is determined by HPLC of the
     coupling products and d.e. values of threo isomers are measured to 20
     .apprx. 95% by 1H NMR. A series of factors such as oxidative coupling
     agents, solvents, bases, which affect coupling reaction have been
     investigated.
ST
     asym oxidative coupling camphor imine carbanion
     Coupling reaction
IT
     Oxidation
        (stereoselective, asym. oxidative coupling reaction of (+)-camphor
        imine carbanions)
IT
     63765-03-7
                  163252-20-8
     RL: RCT (Reactant); RACT (Reactant or reagent)
        (asym. oxidative coupling reaction of (+)-camphor imine carbanions)
TT
     137359-92-3P 163252-19-5P 163252-21-9P
     RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT
     (Reactant or reagent)
        (asym. oxidative coupling reaction of (+)-camphor imine carbanions)
     29841-69-8P 137767-94-3P
                               159928-74-2P
TT
     RL: SPN (Synthetic preparation); PREP (Preparation)
        (asym. oxidative coupling reaction of (+)-camphor imine carbanions)
     137359-92-3P 163252-19-5P 163252-21-9P
     RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT
     (Reactant or reagent)
        (asym. oxidative coupling reaction of (+)-camphor imine carbanions)
ΡN
     137359-92-3 HCAPLUS
     1,2-Ethanediamine, 1,2-diphenyl-N,N'-bis(1,7,7-trimethylbicyclo[2.2.1]hept-
CN
     2-ylidene)-, [1R-[1.alpha.,2E[1S*,2S*(1R*,2E,4R*)],4.alpha.]]- (9CI) (CA
     INDEX NAME)
```

Absolute stereochemistry. Double bond geometry as shown.

RN 163252-19-5 HCAPLUS 1,2-Ethanediamine, 1,2-di-2-pyridinyl-N,N'-bis(1,7,7-trimethylbicyclo[2.2.1]hept-2-ylidene)-, [1R-[1.alpha.,2E[1R\*,2R\*(1R\*,2E,4 CN R\*)],4.alpha.]]- (9CI) (CA INDEX NAME)

Absolute stereochemistry. Rotation (-). Double bond geometry as shown.

RN 163252-21-9 HCAPLUS

1,2-Ethanediamine, 1,2-di-2-pyridinyl-N,N'-bis(1,7,7-trimethylbicyclo[2.2.1]hept-2-ylidene)-, [1R-[1.alpha.,2E[1R\*,2S\*(1R\*,2E,4 CN R\*)],4.alpha.]]- (9CI) (CA INDEX NAME)

Absolute stereochemistry. Double bond geometry as shown.

IT 137767-94-3P

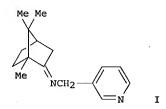
RL: SPN (Synthetic preparation); PREP (Preparation) (asym. oxidative coupling reaction of (+)-camphor imine carbanions) 137767-94-3 HCAPLUS

RN

1,2-Ethanediamine, 1,2-diphenyl-N,N'-bis(1,7,7-trimethylbicyclo[2.2.1]hept-CN 2-ylidene)-, [1R-[1.alpha., 2E[1R\*, 2S\*(1R\*, 2E, 4R\*)], 4.alpha.]]- (9CI) (CA INDEX NAME)

Absolute stereochemistry. Double bond geometry as shown.

L49 ANSWER 9 OF 27 HCAPLUS COPYRIGHT 2004 ACS on STN 1995:182122 HCAPLUS AΝ DN 122:55868 Entered STN: 11 Nov 1994 ΤI Asymmetric synthesis. XX: Asymmetric oxidative coupling reaction of imine carbanions via (+)-camphor chiral template ΑU Liu, Guilan; Hu, Wenhao; Ma, Yuzi; Jiang, Yaozhong; Yang, Teng-Kuei CS Chengdu Inst. Org. Chem., Acad. Sin., Chengdu, 610015, Peop. Rep. China Synthetic Communications (1994), 24(21), 3115-22 CODEN: SYNCAV; ISSN: 0039-7911 PB Dekker DT Journal English LΑ 27-16 (Heterocyclic Compounds (One Hetero Atom)) CCos CASREACT 122:55868



GI

AB The asym. coupling reaction of (+)-camphor imine I using a variety of oxidative coupling agents is described. The threo products are isolated with 80-95% d.e. When FeCl3 or 1,2-dibromoethane is used as oxidative coupling agents, a 93:7 threo:erythro ratio with a d.e. for the threo compound of 95% is obtained.

ST camphor imine asym oxidative coupling

IT Asymmetric synthesis and induction

(asym. oxidative coupling reaction of imine carbanions in presence of FeCl3 or 1,2-dibromoethane)

IT Imines

RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)

(asym. oxidative coupling reaction of imine carbanions via (+)-camphor chiral template)

IT Bond formation

(carbon-carbon, by asym. oxidative coupling reaction of imine carbanions via (+)-camphor chiral template)

IT Coupling reaction catalysts

(oxidative, asym. oxidative coupling reaction of imine carbanions in presence of FeCl3 or 1,2-dibromoethane)

IT Coupling reaction

(oxidative, asym. oxidative coupling reaction of imine carbanions via (+)-camphor chiral template)

IT 106-93-4, 1,2-Dibromoethane 7553-56-2, Iodine, uses 7705-08-0, Iron
 trichloride, uses 7726-95-6, Bromine, uses 15158-11-9, Copper 2+, uses
 RL: CAT (Catalyst use); USES (Uses)

(asym. oxidative coupling reaction of imine carbanions via (+)-camphor chiral template)

IT 464-49-3, (+)-Camphor 3731-51-9, 2-Aminomethylpyridine RL: RCT (Reactant); RACT (Reactant or reagent)

(asym. oxidative coupling reaction of imine carbanions via (+)-camphor chiral template)

IT 159928-72-0P 159928-73-1P

RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent) (asym. oxidative coupling reaction of imine carbanions via (+)-camphor chiral template) 20717-86-6 IT RL: CAT (Catalyst use); USES (Uses) (failed reaction; asym. oxidative coupling reaction of imine carbanions via (+)-camphor chiral template) 159928-74-2P IT RL: SPN (Synthetic preparation); PREP (Preparation) (preparation of) 159928-73-1P RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent) (asym. oxidative coupling reaction of imine carbanions via (+)-camphor chiral template) 159928-73-1 HCAPLUS RN 1,2-Ethanediamine, 1,2-di-2-pyridinyl-N,N'-bis(1,7,7-CN

trimethylbicyclo[2.2.1]hept-2-ylidene) - (9CI) (CA INDEX NAME)

L49 ANSWER 10 OF 27 HCAPLUS COPYRIGHT 2004 ACS on STN AN 1995:55138 HCAPLUS

DN 123:33610

ED Entered STN: 08 Nov 1994

TI Stereospecific Synthesis of Phosphonate Analogs of Diaminopimelic Acid (DAP), Their Interaction with DAP Enzymes, and Antibacterial Activity of Peptide Derivatives

AU Song, Yonghong; Niederer, Daniel; Lane-Bell, Patricia M.; Lam, Lister K. P.; Crawley, Suzanne; Palcic, Monica M.; Pickard, Michael A.; Pruess, David L.; Vederas, John C.

CS Department of Chemistry, University of Alberta, Edmonton, AB, T6G 2G2,

SO Journal of Organic Chemistry (1994), 59(19), 5784-93 CODEN: JOCEAH; ISSN: 0022-3263

DT Journal

LA English

CC 34-3 (Amino Acids, Peptides, and Proteins) Section cross-reference(s): 7, 10, 29

OS CASREACT 123:33610

\* STRUCTURE DIAGRAM TOO LARGE FOR DISPLAY - AVAILABLE VIA OFFLINE PRINT \*

ABB Analogs of diaminopimelic acid (DAP) in which the carboxyl groups are replaced with phosphonic acid moieties were synthesized as pure stereoisomers, examined as inhibitors of three DAP enzymes, and tested as antibacterial agents. Condensation of the enolate of imidazolidinone I with 1,3-dibromopropane stereoselectively gave the expected monobromide II, which was used to alkylate (-)-camphor imine III to yield a 4:1 mixture of diastereomers 1R-IV and 1S-IV, resp. Separation and hydrolytic deprotection gave stereochem. pure (1,5-diamino-5-carboxypentyl) phosphonic acids (1R,5S)-V and (1S,5S)-V. An analogous approach employing (+)-camphor imine VI and monobromide II also allowed synthesis of (1R,5S)-V and (1S,5S)-V, but in a reversed ratio (ca. 2:3). The pure (1R,5R)-V and (1S,5R)-V could be made by a similar procedure using the R-enantiomer of I, 1,3-dibromopropane, and III. A DAP bis-phosphonate analog VII, in which both carboxyl groups are replaced, was synthesized as a mixture of all possible isomers by condensation of 2 equiv of the enolate of imine III or VI with 1,3-dibromopropane followed by hydrolysis. A series of di- and

tripeptides of individual P-DAP isomers with L-alanine were synthesized to enhance transport into bacterial cells for antimicrobial tests.

Condensation of L-alanine N-carboxyanhydride with individual P-DAP isomers (1R,5S)-, (1S,5S)-, (1R,5R)- and (1S,5R)-V in aqueous Na2CO3/DMF gave acylation only on the amino group adjacent to the carboxyl to generate the appropriate dipeptides. Acylation of P-DAP isomers (1R,5S)- and (1S,5S)-V with Boc-L-Ala-L-Ala proceeded similarly to give, after deprotection, the corresponding tripeptides. The P-DAP isomers were generally weak competitive inhibitors of purified DAP decarboxylase from wheat germ (Triticum vulgaris), DAP dehydrogenase from Bacillus sphaericus, and DAP epimerase from Escherichia coli. P-DAP (1S,5S)-V has the strongest effect on the decarboxylase and epimerase, and its enantiomer (1R,5R)-V is the strongest inhibitor of the dehydrogenase. Antibacterial tests show that the P-DAP isomers display negligible activity except against Salmonella typhimurium LT-2. (1S,5S)-V is the most active isomer and its inhibition is reversed by DAP.

ST stereospecific synthesis diaminopimelic acid phosphonate analog; aminopimelic acid phosphonate analog stereospecific synthesis; pimelic acid diamino phosphonate analog; enzyme diaminopimelic acid phosphonate analog; peptide diaminopimelic phosphonate analog prepn antibacterial IT Enzymes

RL: BAC (Biological activity or effector, except adverse); BSU (Biological study, unclassified); BIOL (Biological study)

(DAP; stereospecific synthesis of phosphonate analogs of diaminopimelic acid and their interaction with DAP Enzymes)

IT Bactericides, Disinfectants, and Antiseptics

(preparation of peptide derivs. of diaminopimelic acid phosphonate analogs and their antibacterial activity)

IT Peptides, preparation

RL: BAC (Biological activity or effector, except adverse); BSU (Biological study, unclassified); SPN (Synthetic preparation); BIOL (Biological study); PREP (Preparation)

(phosphono-, preparation of peptide derivs. of diaminopimelic acid phosphonate analogs and their antibacterial activity)

IT Synthesis

IT

(stereoselective, stereospecific synthesis of phosphonate analogs of diaminopimelic acid and their interaction with DAP Enzymes)

163705-98-4P 163705-99-5P 163877-32-5P 163877-33-6P RL: BAC (Biological activity or effector, except adverse); BSU (Biological study, unclassified); SPN (Synthetic preparation); BIOL (Biological study); PREP (Preparation)

(preparation of peptide derivs. of diaminopimelic acid phosphonate analogs and their antibacterial activity)

IT 1948-31-8 2224-52-4 163706-00-1

RL: RCT (Reactant); RACT (Reactant or reagent)

(preparation of peptide derivs. of diaminopimelic acid phosphonate analogs and their antibacterial activity)

IT 27317-69-7P 39743-84-5P 163705-97-3P 163877-29-0P 163877-30-3P 163877-31-4P

RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)

(preparation of peptide derivs. of diaminopimelic acid phosphonate analogs and their antibacterial activity)

IT 9024-22-0 9024-75-3 60894-21-5

RL: BAC (Biological activity or effector, except adverse); BSU (Biological study, unclassified); BIOL (Biological study)

(stereospecific synthesis of phosphonate analogs of diaminopimelic acid and their interaction with DAP Enzymes)

IT 163877-14-3P 163877-15-4P 163877-18-7P 163877-19-8P RL: BAC (Biological activity or effector, except adverse); BSU (Biological study, unclassified); RCT (Reactant); SPN (Synthetic preparation); BIOL (Biological study); PREP (Preparation); RACT (Reactant or reagent)

(stereospecific synthesis of phosphonate analogs of diaminopimelic acid and their interaction with DAP Enzymes)

583-93-7DP, phosphonate analogs 13598-36-2DP, Phosphonic acid, diaminopimelic acid analogs 137407-98-8P 163877-23-4P 163877-28-9P RL: BAC (Biological activity or effector, except adverse); BSU (Biological study, unclassified); SPN (Synthetic preparation); BIOL (Biological study); PREP (Preparation)

(stereospecific synthesis of phosphonate analogs of diaminopimelic acid and their interaction with DAP Enzymes)

IT 109-64-8, 1.3-Dibromopropane 101055-56-5 101055-57-6 104549-54-4 139563-58-9

RL: RCT (Reactant); RACT (Reactant or reagent)
 (stereospecific synthesis of phosphonate analogs of diaminopimelic acid
 and their interaction with DAP Enzymes)

IT 163705-93-9P 163705-94-0P 163705-95-1P 163705-96-2P 163877-13-2P 163877-16-5P 163877-17-6P 163877-20-1P 163877-21-2P 163877-22-3P 163877-24-5P 163877-25-6P 163877-26-7P 163877-27-8P RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent) (stereospecific synthesis of phosphonate analogs of diaminopimelic acid and their interaction with DAP Enzymes) 163705-96-2P 163877-22-3P 163877-24-5P IT 163877-25-6P 163877-26-7P 163877-27-8P RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent) (stereospecific synthesis of phosphonate analogs of diaminopimelic acid and their interaction with DAP Enzymes) RN163705-96-2 HCAPLUS Phosphonic acid, [1,5-bis[(1,7,7-trimethylbicyclo[2.2.1]hept-2ylidene)amino]-1,5-pentanediyl]bis-, tetraethyl ester, [1S-[1.alpha.,2[iS\*,5S\*(1'R\*,4'R\*)],4.alpha.]]- (9CI) (CA INDEX NAME)

Absolute stereochemistry.

Double bond geometry unknown.

RN 163877-22-3 HCAPLUS
CN Phosphonic acid, [1,5-bis[(1,7,7-trimethylbicyclo[2.2.1]hept-2-ylidene)amino]-1,5-pentanediyl]bis-, tetraethyl ester, [1R-[1.alpha.,2[1R\*,5R\*(1R\*,4R\*)],4.alpha.]]- (9CI) (CA INDEX NAME)

Absolute stereochemistry.

Double bond geometry unknown.

RN 163877-24-5 HCAPLUS
CN Phosphonic acid, [1,5-bis[(1,7,7-trimethylbicyclo[2.2.1]hept-2-ylidene)amino]-1,5-pentanediyl]bis-, tetraethyl ester,
[1S-[1.alpha.,2[1R\*,5R\*(1R\*,4R\*)],4.alpha.]]- (9CI) (CA INDEX NAME)

Absolute stereochemistry. Double bond geometry unknown.

RN 163877-25-6 HCAPLUS CN Phosphonic acid, [1,5-bis[(1,7,7-trimethylbicyclo[2.2.1]hept-2ylidene)amino]-1,5-pentanediyl]bis-, tetraethyl ester,
[1S-[1.alpha.,2[1R\*,5S\*(1R\*,4R\*)],4.alpha.]]- (9CI) (CA INDEX NAME)

Absolute stereochemistry.

Double bond geometry unknown.

RN 163877-26-7 HCAPLUS

CN Phosphonic acid, [1,5-bis[(1,7,7-trimethylbicyclo[2.2.1]hept-2-ylidene)amino]-1,5-pentanediyl]bis-, tetraethyl ester, [1R-[1.alpha.,2[1S\*,5S\*(1R\*,4R\*)],4.alpha.]]- (9CI) (CA INDEX NAME)

Absolute stereochemistry.

Double bond geometry unknown.

Me 
$$R$$
 EtO  $R$  OEt  $R$  Me  $R$  Me  $R$  Me  $R$  Me  $R$  Me

RN 163877-27-8 HCAPLUS

Phosphonic acid, [1,5-bis[(1,7,7-trimethylbicyclo[2.2.1]hept-2-ylidene)amino]-1,5-pentanediyl]bis-, tetraethyl ester, [1R-[1.alpha.,2[1R\*,5S\*(1R\*,4R\*)],4.alpha.]]- (9CI) (CA INDEX NAME)

Absolute stereochemistry.

Double bond geometry unknown.

- L49 ANSWER 11 OF 27 HCAPLUS COPYRIGHT 2004 ACS on STN
- AN 1994:630119 HCAPLUS
- DN 121:230119
- ED Entered STN: 12 Nov 1994
- TI Valence isomerization of amides of 3-phenylnorbornadiene-2-carboxylic acid
- AU Chernouvamov, V. A.; Dubonosov, A. D.; Popova, L. L.; Galichev, S. V.;
  - Borodkin, G. S.; Bren, V. A.; Minkin, V. I.
- CS Rostov. Gos. Univ., Rostov, Russia
- SO Zhurnal Organicheskoi Khimii (1993), 29(11), 2148-52
- CODEN: ZORKAE; ISSN: 0514-7492
- DT Journal
- LA Russian
- CC 22-6 (Physical Organic Chemistry)
- Section cross-reference(s): 52

GI

AB Photoisomerization of norbornadienes I [R = (un) substituted Ph, .alpha.-and .beta.-naphthyl] at .lambda.max of the long-wavelength absorption (313 nm) afforded quadricyclanes II with quantum yields of up to 0.71 (for R = C6H4CO2Et-4). Electron-accepting R increase, and electron-donating substituents decrease the quantum yield relative to R = Ph; however, the limiting .lambda. values for I and II become similar for electron-accepting R, which is undesirable for solar energy storage. II are converted to I in presence of MoO3.

ST arylamide phenylnorbornadienecarboxylic acid photochem valence isomerization; quadricyclane; substituent effect photoisomerization norbornadiene deriv

IT Isomerization catalysts

(molybdenum trioxide, for arylamides of phenylquadricyclanecarboxylic acid to norbornadienes)

IT Isomerization

Kinetics of isomerization

(of arylamides of phenylquadricyclanecarboxylic acid in presence of molybdenum trioxide)

IT Substituent effect

(on photochem. valence isomerization of 3-phenylnorbornadiene-2carboxylic acid arylamides)

IT Amides, reactions

RL: RCT (Reactant); RACT (Reactant or reagent)

(aryl, of 3-phenylnorbornadiene-2-carboxylic acid, photochem. valence isomerization of, substituent effect on)

IT Isomerization

(valence, photochem., of arylamides of 3-phenylnorbornadiene-2-carboxylic acid, substituent effect on)

IT 542-92-7, Cyclopentadiene, reactions

RL: RCT (Reactant); RACT (Reactant or reagent)

(Diels-Alder cycloaddn. with phenylpropiolic acid chloride)

IT 62-53-3, Aniline, reactions 91-59-8, beta.-Naphthylamine 94-09-7,
4-(Ethoxycarbonyl)aniline 95-53-4, 2-Methylaniline, reactions 99-09-2,
3-Nitroaniline 99-92-3, 4-Acetylaniline 104-94-9, 4-Methoxyaniline
106-49-0, 4-Methylaniline, reactions 119-90-4, 4,4'-Diamino-3,3'dimethoxybiphenyl 134-32-7, alpha.-Naphthylamine
RL: RCT (Reactant); RACT (Reactant or reagent)

(amidation with, of 3-phenylnorbornadiene-2-carboxylic acid chloride)

IT 1313-27-5, Molybdenum oxide (MoO3), uses

RL: CAT (Catalyst use); USES (Uses)

(catalysts, for isomerization of phenylquadricyclanecarboxylic acid arylamides to norbornadiene)

IT 637-44-5, Phenylpropiolic acid

RL: PRP (Properties)

(conversion to acid chloride)

IT 7299-58-3P, Phenylpropiolic acid chloride

RL: SPN (Synthetic preparation); PREP (Preparation)

(preparation and Diels-Alder cycloaddn. with cyclopentadiene)

IT 158198-05-1P, 3-Phenylnorbornadiene-2-carboxylic acid chloride
 RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT

(Reactant or reagent)
 (preparation and amidation of, with arylamines)

(preparation and amidation of, with arylamines)
IT 158197-96-7P 158197-97-8P 158197-98-9P 158197-99-0P 158198-00-6P 158198-01-7P 158198-02-8P 158198-03-9P 158198-04-0P

RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)

(preparation and isomerization of, to norbornadiene derivative in presence of molybdenum trioxide)

TT 158197-86-5P 158197-87-6P 158197-88-7P 158197-89-8P 158197-90-1P

158197-91-2P 158197-92-3P 158197-94-5P 158197-95-6P RL: RCT (Reactant): SPN (Synthetic preparation): PREP (Preparation); R

RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)

(preparation and photochem. valence isomerization of, to quadricyclane derivative)

IT 158197-93-4P

RL: SPN (Synthetic preparation); PREP (Preparation)
 (preparation of)

ANSWER 12 OF 27 HCAPLUS COPYRIGHT 2004 ACS on STN L49 1994:620076 HCAPLUS AN DN 121:220076 Entered STN: 29 Oct 1994 ED A general method of promoting agostic interactions (Ru-Ha-C) using azine ΤI ΑU Perea, Sarath D.; Shaw, Bernard L. Sch. Chem., Univ. Leeds, Leeds, LS2 9JT, UK CS Journal of the Chemical Society, Chemical Communications (1994), (10), SO 1201-2 CODEN: JCCCAT; ISSN: 0022-4936  $\mathbf{DT}$ Journal English LA 78-7 (Inorganic Chemicals and Reactions) CC Section cross-reference(s): 29 GΙ

$$\begin{array}{c|c}
R^1 & R \\
\parallel & N \\
N & Ph \\
Me & C & CH_2
\end{array}$$
Me Me Me Me Ph Me

AB Treatment of [RuCl2(PPh3)3] with azine phosphines (I R = CMe3, C6H4NMe2-4-me, CH:CHPh, R1 = Me, H, Me, resp.) gives complexes showing strong agostic interactions between Ru and C-H bonds of tert-Bu, Me, aryl or alkenyl groups in dynamic systems. For example, all 9 hydrogens of a tert-Bu group are agostically interacting with Ru on the NMR timescale at 20.degree..

ST ruthenium azine phosphine chloro prepn agostic; agostic bond ruthenium

st ruthenium azine phosphine chloro prepn agostic; agostic bond ruthenium azine phosphine complex

IT Bond

(agostic, in ruthenium azine phosphine chloro complexes, general preparation method for)

IT 156857-19-1

RL: RCT (Reactant); RACT (Reactant or reagent)

(butylation and reaction of, with diphenylphosphine chloride)

IT 75-97-8 100-10-7, 4-Dimethylaminobenzaldehyde 122-57-6, Benzylidene

RL: RCT (Reactant); RACT (Reactant or reagent)

(condensation reaction of, with phosphine hydrazone)

IT 144116-28-9

RL: RCT (Reactant); RACT (Reactant or reagent)

(condensation reaction of, with with aldehydes or ketones)

IT 156783-24-3P

RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)

Page 32

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Kumar 10/612609
                     (preparation and reaction of, with ruthenium chloro phosphine complex)
            155606-61-4P 156783-25-4P 156783-26-5P 156783-27-6P
            RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT
             (Reactant or reagent)
                     (preparation and reaction of, with with ruthenium chloro phosphine complex)
            158273-99-5P
                                                  158274-00-1P 158274-01-2P
                                                                                                                              158274-02-3P 158274-03-4P
            158308-33-9P
            RL: SPN (Synthetic preparation); PREP (Preparation)
                     (preparation of)
            15529-49-4, Dichlorotris(triphenylphosphine)ruthenium
            RL: RCT (Reactant); RACT (Reactant or reagent)
                     (reaction of, with azine phosphines)
            1079-66-9, Diphenylphosphine chloride
TT
            RL: RCT (Reactant); RACT (Reactant or reagent)
                     (reaction of, with butylated camphorazine)
            143627-09-2
            RL: RCT (Reactant); RACT (Reactant or reagent)
                     (reaction of, with ruthenium chloro phosphine complex)
IT
            156857-19-1
            RL: RCT (Reactant); RACT (Reactant or reagent)
                     (butylation and reaction of, with diphenylphosphine chloride)
            156857-19-1 HCAPLUS
RN
            {\tt Bicyclo[2.2.1] heptan-2-one, 1,7,7-trimethyl-, (1,7,7-trimethyl-, (1,7,7-trimethyl-,
CN
             trimethylbicyclo[2.2.1]hept-2-ylidene)hydrazone, [1S-
             [1.alpha.,2(1R*,4R*),4.alpha.]]- (9CI) (CA INDEX NAME)
            156783-25-4P
            RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT
             (Reactant or reagent)
```

(preparation and reaction of, with with ruthenium chloro phosphine complex) 156783-25-4 HCAPLUS RN Bicyclo[2.2.1]heptan-2-one, 3-(diphenylphosphino)-1,7,7-trimethyl-, CN (1,7,7-trimethylbicyclo[2.2.1]hept-2-ylidene)hydrazone, [1S-[1.alpha.,2(1R\*,4R\*),3.beta.,4.alpha.]]- (9CI) (CA INDEX NAME)

L49

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AN
     1993:233794 HCAPLUS
DN
     118:233794
     Entered STN: 12 Jun 1993
ED
     Studies on the asymmetric synthesis of (R)-.alpha.-alkylfurfurylamines
TI
     Liu, Guilan; Hu, Wenhao; Deng, Jingen; Mi, Aiqiao; Jiang, Yaozhong
ΑU
     Chengdu Inst. Org. Chem., Acad. Sin., Chengdu, 610015, Peop. Rep. China
CS
so
     Huaxue Xuebao (1993), 51(1), 73-8
     CODEN: HHHPA4; ISSN: 0567-7351
DT
     Journal
LΑ
     Chinese
     27-6 (Heterocyclic Compounds (One Hetero Atom))
os
     CASREACT 118:233794
```

ANSWER 13 OF 27 HCAPLUS COPYRIGHT 2004 ACS on STN

AB (R) - .alpha. - Alkyl-furfurylamines are synthesized by asym. alkylation of (+)-camphor ketimine I obtained from furfurylamine. The diastereoselectivities ranging from 5.apprx.67% are determined by 1H NMR spectra of alkylation products. Using 3-diiodopropane and dibromoxylane as alkylating reagents, diimine derivs. are formed. However, 1,2-dibromoethane gives 2 coupling products. furfurylamine alpha alkyl asym synthesis; camphor ketimine furfurylamine asym alkylation IT Asymmetric synthesis and induction (of .alpha.-alkylfurfurylamines) IT Alkvlation (stereoselective, of furfurylamine derivative) 91-13-4 IT 74-88-4, reactions 75-26-3, Isopropyl bromide o-Bis(bromomethyl)benzene 100-39-0, Benzyl bromide 106-93-4, 1,2-Dibromoethane 106-95-6, Allyl bromide, reactions 627-31-6, 1.3-Diiodopropane 824-94-2, p-Methoxybenzyl chloride RL: RCT (Reactant); RACT (Reactant or reagent) (alkylation by, of furfurylamine derivative) 132523-42-3 RL: RCT (Reactant); RACT (Reactant or reagent) (asym. alkylation of) 132523-46-7P 132523-48-9P 132523-50-3P 132523-52-5P IT 132523-44-5P RL: SPN (Synthetic preparation); PREP (Preparation) (asym. synthesis of) IT 147356-49-8P RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent) (preparation and oxidation of) 132523-45-6P 132523-47-8P 132523-49-0P 132523-51-4P 132523-43-4P RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent) (preparation and reaction of, with hydroxylamine)

CN 1,5-Pentanediamine, 1,5-di-2-furanyl-N,N'-bis(1,7,7-trimethylbicyclo[2.2.1]hept-2-ylidene)-, [1R-[1.alpha.,2[1S\*,5S\*(1R\*,4R\*)],4.alpha.]]- (9CI) (CA INDEX NAME)

RN132617-81-3 HCAPLUS 1,5-Pentanediamine, 1,5-di-2-furanyl-N,N'-bis(1,7,7-trimethylbicyclo[2.2.1]hept-2-ylidene)-, [1R-[1.alpha.,2[1R\*,5R\*(1R\*,4R\*)] ,4.alpha.]]- (9CI) (CA INDEX NAME)

ANSWER 14 OF 27 HCAPLUS COPYRIGHT 2004 ACS on STN L49

ΑN 1992:6747 HCAPLUS

DN 116:6747

Entered STN: 11 Jan 1992 ED

Asymmetric synthesis. XIV. TiCl(OCHMe2)3-promoted asymmetric coupling TI reaction of d-camphor ketimine anion

UA Jiang, Yaozhong; Hu, Wenhao; Deng, Jingen; Liu, Giulan

CS

Chengdu Inst. Org. Chem., Acad. Sin., Chengdu, 610015, Peop. Rep. China Synthetic Communications (1991), 21(17), 1755-61 SO CODEN: SYNCAV; ISSN: 0039-7911

 $\mathbf{DT}$ Journal

English LΑ

CC 30-10 (Terpenes and Terpenoids)

os CASREACT 116:6747 GI

NH2 NH2

- Optically active 1,2-diphenylethylenediamine (I) is obtained by asym. AB oxidative coupling reaction of d-camphor ketimine anion II. Among various oxidating agents, TiCl(OCHMe)3 is better than I2, Br2, CuCl2, FeCl3 and BrCH2CH2Br.
- chlorotitanium triisopropoxide protonated oxidative coupling; camphor ST ketimine dimerization oxidative coupling; diphenylethylenediamine; ethylenediamine diphenyl; asym oxidative coupling camphor ketimine IT Oxidizing agents

(chlorotitanium isopropoxide for camphor ketimine)

Stereochemistry IT

(of chlorotitanium isopropoxide-promoted oxidative coupling of camphor

Asymmetric synthesis and induction ΙT

(of diphenylethylenediamine via oxidative coupling of camphor ketimine)

IT Synthons

(chiral, camphor as auxiliary in asym. oxidative coupling reaction)

IT Coupling reaction

(oxidative, chlorotitanium isopropoxide-promoted, of camphor ketimine)

IT 63765-03-7

RL: PRP (Properties)

(lithiation and chlorotitanium isopropoxide-promoted oxidative coupling of)

IT 106-93-4, 1,2-Dibromoethane 7447-39-4, Cupric chloride, reactions 7553-56-2, Iodine, reactions 7705-08-0, Ferric chloride, reactions 7726-95-6, Bromine, reactions 20717-86-6, Chlorotitanium triisopropoxide RL: RCT (Reactant); RACT (Reactant or reagent) (oxidizing agent for asym. coupling of camphor ketimine)

137359-91-2P

RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)

(preparation and chlorotitanium isopropoxide-promoted oxidative coupling of)

29841-69-8P 137767-94-3P

RL: PRP (Properties); SPN (Synthetic preparation); PREP (Preparation) (preparation and crystal structure of)

137359-92-3P

RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)

(preparation and reaction of, with hydroxylamine)

IT 137767-94-3P

RL: PRP (Properties); SPN (Synthetic preparation); PREP (Preparation) (preparation and crystal structure of)

RN 137767-94-3 HCAPLUS

1,2-Ethanediamine, 1,2-diphenyl-N,N'-bis(1,7,7-trimethylbicyclo[2.2.1]hept-CN 2-ylidene)-, [1R-[1.alpha.,2E[1R\*,2S\*(1R\*,2E,4R\*)],4.alpha.]]- (9CI) (CA

Absolute stereochemistry. Double bond geometry as shown.

IT 137359-92-3P

RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)

(preparation and reaction of, with hydroxylamine)

137359-92-3 HCAPLUS

CN 1,2-Ethanediamine, 1,2-diphenyl-N,N'-bis(1,7,7-trimethylbicyclo[2.2.1]hept-2-ylidene)-, [1R-[1.alpha.,2E[1S\*,2S\*(1R\*,2E,4R\*)],4.alpha.]]- (9CI) (CA INDEX NAME)

Absolute stereochemistry. Double bond geometry as shown.

- ANSWER 15 OF 27 HCAPLUS COPYRIGHT 2004 ACS on STN L49
- 1991:153790 HCAPLUS AN
- DN 114:153790
- Entered STN: 19 Apr 1991 ED
- ΤI Photochemistry of bichromophoric molecules with camphor structure. II: The photochemistry of 3-diazocamphor
- AU Rau, H.; Bokel, M.
- CS Inst. Chem., Univ. Hohenheim, Stuttgart, 7000/70, Germany
- so Journal of Photochemistry and Photobiology, A: Chemistry (1990), 53(3), 311-22
- CODEN: JPPCEJ; ISSN: 1010-6030
- DT Journal

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LΑ
     English
CC
     74-1 (Radiation Chemistry, Photochemistry, and Photographic and Other
     Reprographic Processes)
     Section cross-reference(s): 22
     Irradiation of 3-diazocamphor (I) in ethanol mainly yields an ester, which is
     in agreement with the literature. In addition camphor-3-diazirine compound is
     formed with a 25 .+-. 5% yield. A small amount of camphor is detected at
     .lambda.irr >400 nm and a trace of camphorquinone azine at .lambda.irr =
     313 nm. In n-hexane at .lambda.irr >400 nm the main product is the
     diazirine compound; some tricyclanone and enedione are also formed. The
     diazirine is thermally rather stable but reacts very slowly (t1/2 = 16 \text{ h})
     at 333 K in EtOH) to form back I with a 20% yield. The diazirine reacts on irradiation with a quantum yield of 70 .+-. 10%. Direct N2 extrusion and
     reformation of diazocamphor (37 .+-. 5%) are parallel reactions.
ST
     diazocamphor photochem diazo diazirine isomerization; photolysis
     diazocamphor nitrogen elimination
IT
     Solvent effect
        (in photolysis of diazocamphor)
IT
     Photolysis
         (of diazocamphor, solvent effect on product formation in)
IT
     Isomerization
        (photochem., diazirine to diazomethane, in photolysis of diazocamphor)
IT
     Elimination reaction
        (photochem., of nitrogen, in photolysis of diazocamphor)
     76-22-2P, Camphor 132736-29-9P 132757-99-4P 132830-79-6P
TT
     RL: FORM (Formation, nonpreparative); PREP (Preparation)
        (formation of, in photolysis of diazocamphor)
     132831-80-2P
     RL: FORM (Formation, nonpreparative); PREP (Preparation)
        (formation of, in photolysis of diazocamphor in ethanol)
IT
     875-99-0P, Tricyclanone
                                94167-43-8P
     RL: FORM (Formation, nonpreparative); PREP (Preparation)
        (formation of, in photolysis of diazocamphor in hexane solution)
IT
     132736-28-8P
     RL: FORM (Formation, nonpreparative); PREP (Preparation)
     (formation of, in photolysis of diazocamphor, photochem. of) 64-17-5, Ethanol, uses and miscellaneous 110-54-3, Hexane, uses and
     miscellaneous
     RL: USES (Uses)
        (photolysis of diazocamphor in solution of, products from)
IT
     14487-70-8, 3-Diazocamphor
     RL: RCT (Reactant); RACT (Reactant or reagent)
        (photolysis of, solvent effect on isomerization and nitrogen
        elimination in)
TT
     132830-79-6P
     RL: FORM (Formation, nonpreparative); PREP (Preparation)
        (formation of, in photolysis of diazocamphor)
     132830-79-6 HCAPLUS
RN
CN
     Bicyclo[2.2.1] heptane-2,3-dione, 1,7,7-trimethyl-, 3-[(4,7,7-trimethyl-3-
     oxobicyclo[2.2.1]hept-2-ylidene)hydrazone], [1.alpha.,3Z(1S*,2Z,4R*),4.alp
     ha.] - (9CI) (CA INDEX NAME)
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1.49
    ANSWER 16 OF 27 HCAPLUS COPYRIGHT 2004 ACS on STN
     1991:122728 HCAPLUS
ΑN
     114:122728
ED
     Entered STN: 06 Apr 1991
TI
     Asymmetric synthesis. XI. Stereoselective synthesis of
     .alpha.-alkyl-2-furfurylamines via d-camphor ketimine intermediate
ΑU
     Jiang, Yaozhong; Deng, Jingen; Hu, Wenhao; Liu, Giulan; Mi, Aiqiao
CS
     Chengdu Inst. Org. Chem., Acad. Sin., Chengdu, 610015, Peop. Rep. China
     Synthetic Communications (1990), 20(19), 3077-83
SO
     CODEN: SYNCAV; ISSN: 0039-7911
DТ
     Journal
LА
     English
     30-10 (Terpenes and Terpenoids)
CC
     CASREACT 114:122728
```

(R)-.alpha.-Alkyl-2-furfurylamines I (R = Me, CH2:CHCH2, Me2CH, PhCH2, AB p-MeOC6H4CH2), ranging from 5-67% d.e., are obtained by asym. alkylation of d-camphor ketimine II. Using 1,3-diiodopropane and dibromoxylene as alkylating reagents, diimine derivs. III [X = CH2CH2CH2, 1,2-C6H4(CH2)2], resp. are formed. However, 1,2-dibromoethane gives coupling product IV. ST asym synthesis alkylfurfurylamine alkylated furfurylamine; camphor ketimine alkylation stereoselectivity IT Stereochemistry (of alkylation of D-camphor N-furfurylketimine) IT Asymmetric synthesis and induction (of .alpha.-alkylfurfurylamine from d-camphor) IT Synthons (chiral, d-camphor for .alpha.-alkylfurfurylamines) IT Alkylation (stereoselective, of D-camphor N-furfurylketimine, .alpha.alkylfurfurylamines via) IT 132523-44-5P 132523-46-7P 132523-48-9P 132523-50-3P 132523-52-5P RL: SPN (Synthetic preparation); PREP (Preparation) (asym. synthesis of) IT 464-49-3, d-Camphor RL: RCT (Reactant); RACT (Reactant or reagent) (condensation of, with furfurylamine) IT 617-89-0, Furfurylamine RL: RCT (Reactant); RACT (Reactant or reagent) (condensation of, with d-camphor) IT 132523-42-3P RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent) (preparation and stereoselective alkylation of) 132523-49-0P 132523-51-4P IT 132523-43-4P 132523-45-6P 132523-47-8P RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent) (preparation and transamination of, with hydroxylamine, .alpha .alkylfurfurylamine by) 132523-36-5P 132523-37-6P IT 132523-35-4P 132617-80-2P 132617-81-3P 132617-82-4P 132617-83-5P 132617-84-6P 132617-85-7P RL: SPN (Synthetic preparation); PREP (Preparation) (stereoselective preparation of, from d-camphor N-furfurylketimine) 132523-35-4P 132523-37-6P 132617-80-2P 132617-81-3P 132617-84-6P 132617-85-7P RL: SPN (Synthetic preparation); PREP (Preparation) (stereoselective preparation of, from d-camphor N-furfurylketimine)

Search done by Noble Jarrell

ΙT

98-86-2, Acetophenone, reactions

```
ANSWER 17 OF 27 HCAPLUS COPYRIGHT 2004 ACS on STN
AN
     1989:231896 HCAPLUS
DN
     110:231896
     Entered STN: 25 Jun 1989
ED
TI
     On the mechanism of formation of azines from hydrazones
     Kolb, Vera M.; Kuffel, Andrew C.; Spiwek, Harry O.; Janota, Timothy E.
ΑU
     Dep. Chem., Univ. Wisconsin Parkside, Kenosha, WI, 531410, USA
CS
SO
     Journal of Organic Chemistry (1989), 54(11), 2771-5
     CODEN: JOCEAH; ISSN: 0022-3263
DT
     Journal
LΑ
     English
CC
     30-10 (Terpenes and Terpenoids)
     Section cross-reference(s): 25
OS
     CASREACT 110:231896
     Treating camphor with N2H4.H2O in EtOH with or without HCl catalyst gave a
AB
     low yield of hydrazone which on standing gave the azine. Conjugated
     ketones such as camphorquinone, PhCOMe, p-O2NC6H4COMe, and p-MeOC6H4COMe
     gave predominantly hydrazones and either no azines or traces of azines.
     2-Adamantanone gave both hydrazone and azine; on standing the mixture was
     converted completely to azine. An addition-elimination mechanism for these
     conversions of hydrazones to azines is questioned.
     terpene ketone hydrazone azine conversion; acetophenone hydrazone azine;
     camphorquinone hydrazone azine; adamantanone hydrazone azine; ketone
     terpene hydrazone azine conversion
     Azines
     Hydrazones
     RL: FORM (Formation, nonpreparative)
        (formation of, from monoterpenoid and aryl ketones)
IT
     Ketones, reactions
     RL: RCT (Reactant); RACT (Reactant or reagent)
        (aryl, reaction of, with hydrazone hydrate, hydrazones and azines from)
     61833-37-2P
IT
                   120443-05-2P
     RL: SPN (Synthetic preparation); PREP (Preparation)
        (preparation and conversion to azine)
     729-43-1P 6310-14-1P 7803-57-8P, Hydrazine hydrate 13466-30-3P 21399-34-8P, 4'-Methoxyacetophenone azine 28153-22-2P 39555-34-5
     21399-34-8P, 4'-Methoxyacetophenone azine 28153-22-2P 3959
2-Adamantanone azine 86707-47-3P 86707-48-4P 120443-06-3P
                                                                  39555-34-5P,
     RL: SPN (Synthetic preparation); PREP (Preparation)
        (preparation of)
     100-06-1, 4'-Methoxyacetophenone
     RL: RCT (Reactant); RACT (Reactant or reagent)
        (reaction of, with hydrazine hydrate hydrazone and azine from)
IT
     464-49-3
                700-58-3, 2-Adamantanone
     RL: RCT (Reactant); RACT (Reactant or reagent)
        (reaction of, with hydrazine hydrate with or without acidic catalysts)
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RL: RCT (Reactant); RACT (Reactant or reagent)
        (reaction of, with hydrazine hydrate, hydrazone and azine from)
     100-19-6, 4'-Nitroacetophenone
     RL: RCT (Reactant); RACT (Reactant or reagent)
        (reaction of, with hydrazine hydrate, hydrazone from)
     RL: RCT (Reactant); RACT (Reactant or reagent)
        (reaction of, with hydrazine hydrate, stereoisomeric hydrazones from)
TT
     120443-06-3P
     RL: SPN (Synthetic preparation); PREP (Preparation)
        (preparation of)
     120443-06-3 HCAPLUS
RN
     Bicyclo[2.2.1]heptan-2-one, 1,7,7-trimethyl-, (1,7,7-
CN
     trimethylbicyclo[2.2.1]hept-2-ylidene)hydrazone, [1S-
     [1.alpha., 2E(1R*, 2E, 4S*), 4.alpha.]] - (9CI) (CA INDEX NAME)
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L49
    ANSWER 18 OF 27 HCAPLUS COPYRIGHT 2004 ACS on STN
     1987:525781 HCAPLUS
DN
     107:125781
ED
     Entered STN: 05 Oct 1987
     Role of metal ions in reactions of .alpha.-bornane-2,3-dione with diamines
ТT
     Kashalkar, R. V.; Mukhedkar, V. A.; Mukhedkar, A. J.
     Dep. Chem., Univ. Poona, Pune, 411 007, India
     Indian Journal of Chemistry, Section A: Inorganic, Physical, Theoretical
     & Analytical (1987), 26A(3), 225-9
     CODEN: IJCADU; ISSN: 0376-4710
DT
     Journal
LΑ
     English
CC
     78-7 (Inorganic Chemicals and Reactions)
     Section cross-reference(s): 24
AB
     Synthesis of diimines of d-bornane-2,3-dione with imine groups at C(2) was
     achieved by condensation of the diamines and d-bornane-2,3-dione in the
     presence of metal ions (Ni2+ and Cu2+). Complexes of these metal ions and
     also of Co2+ and Pd2+ with similar diimine ligands containing imine groups at
     C(3) positions were also prepared and characterized by elemental anal.,
     magnetic susceptibility and spectral (IR, 1H NMR) methods.
     transition metal Schiff diamine bornanedione; diimine bornanedione diamine
     template prepn; nickel diimine bornanedione diamine; copper diimine
     bornanedione diamine; cobalt diimine bornanedione diamine; palladium
     diimine bornanedione diamine
     Schiff bases
     RL: SPN (Synthetic preparation); PREP (Preparation)
        (diamine-d-bornanedione, preparation of, by template condensation)
TT
     Stereochemistry
        (of template condensation reaction of .alpha.-bornanedione with
        diamines in presence of transition metal ions)
IT
     Condensation reaction
        (template, of .alpha.-bornanedione with diamines in presence of
        transition metal ions)
     Transition metals, compounds
IT
        (bornanedione-diamine Schiff-base complexes)
IT
     Amines, reactions
     RL: RCT (Reactant); RACT (Reactant or reagent)
        (di-, template condensation reactions of, with d-bornanedione in
        presence of transition metal ions)
     78-90-0, 1,2-Propanediamine
                                  107-15-3, Ethylenediamine, reactions
                                   110-60-1, 1,4-Butanediamine
     109-76-2, 1,3-Propanediamine
     RL: RCT (Reactant); RACT (Reactant or reagent)
        (condensation reaction of, with d-bornanedione, role of transition
        metal ions in)
     2767-84-2
     RL: RCT (Reactant); RACT (Reactant or reagent)
        (condensation reactions of, with diamines, role of transition metal
        ions in)
     23927-62-0P 109881-45-0P 109881-46-1P
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109881-47-2P 109881-48-3P 109881-49-4P
                             109896-16-4P
                                             109896-17-5P
109881-50-7P 109894-82-8P
                                                               109896-22-2P
               109896-19-7P
                               109896-20-0P
                                               109896-21-1P
109896-18-6P
                                                               109896-27-7P
109896-23-3P
               109896-24-4P
                               109896-25-5P
                                               109896-26-6P
                                                               109896-32-4P
                                               109896-31-3P
109896-28-8P
               109896-29-9P
                               109896-30-2P
109896-33-5P
               109896-34-6P
                               109896-35-7P
                                               109896-36-8P
                                                               109896-37-9P
               109896-39-1P
                               109896-40-4P
                                               109910-78-3P
                                                               110305-33-4P
109896-38-0P
RL: SPN (Synthetic preparation); PREP (Preparation)
   (preparation of)
23927-62-0P 109881-45-0P 109881-46-1P
109881-47-2P 109881-48-3P 109881-49-4P 109881-50-7P 109894-82-8P
RL: SPN (Synthetic preparation); PREP (Preparation)
   (preparation of)
23927-62-0 HCAPLUS
Bicyclo[2.2.1]heptan-2-one, 3,3'-(1,3-propanediyldinitrilo)bis[1,7,7-
trimethyl-, [1.alpha.,3(1'R*,4'S*),4.alpha.]-(+)- (9CI) (CA INDEX NAME)
```

$$\begin{array}{c} \text{Me} \\ \text{Me} \\ \text{Me} \end{array} \begin{array}{c} \text{N} \\ \text{Me} \\ \text{Me} \\ \text{Me} \end{array}$$

RN

CN

RN 109881-45-0 HCAPLUS CN Bicyclo[2.2.1]heptan-2-one, 3,3'-(1,2-ethanediyldinitrilo)bis[1,7,7-trimethyl-, [1S-[1.alpha.,3(1'R\*,4'S\*),4.alpha.]]- (9CI) (CA INDEX NAME)

RN 109881-46-1 HCAPLUS CN Bicyclo[2.2.1]heptan-2-one, 3,3'-(1,2-ethanediyldinitrilo)bis[4,7,7-trimethyl-, [1R-[1.alpha.,3(1'R\*,4'S\*),4.alpha.]]- (9CI) (CA INDEX NAME)

RN 109881-47-2 HCAPLUS
CN Bicyclo[2.2.1]heptan-2-one, 3,3'-[(1-methyl-1,2-ethanediyl)dinitrilo]bis[4,7,7-trimethyl- (9CI) (CA INDEX NAME)

RN 109881-48-3 HCAPLUS CN Bicyclo[2.2.1]heptan-2-one, 3,3'-(1,3-propanediyldinitrilo)bis[4,7,7-trimethyl-, [1R-[1.alpha.,3(1'R\*,4'S\*),4.alpha.]]- (9CI) (CA INDEX NAME)

RN 109881-49-4 HCAPLUS Bicyclo[2.2.1]heptan-2-one, 3,3'-(1,4-butanediyldinitrilo)bis[1,7,7-CN trimethyl-, [1S-[1.alpha.,3(1'R\*,4'S\*),4.alpha.]]- (9CI) (CA INDEX NAME)

109881-50-7 HCAPLUS Bicyclo[2.2.1]heptan-2-one, 3,3'-(1,4-butanediyldinitrilo)bis[4,7,7-CN trimethyl-, [1R-[1.alpha.,3(1'R\*,4'S\*),4.alpha.]]- (9CI) (CA INDEX NAME)

RN 109894-82-8 HCAPLUS Bicyclo[2.2.1]heptan-2-one, 3,3'-[(1-methyl-1,2-CN ethanediyl)dinitrilo]bis[1,7,7-trimethyl- (9CI) (CA INDEX NAME)

L49 ANSWER 19 OF 27 HCAPLUS COPYRIGHT 2004 ACS on STN

1987:195680 HCAPLUS AN

DM 106:195680

ED Entered STN: 13 Jun 1987

Synthesis and valence photoisomerization of naphthyl esters of norbornadienecarboxylic acids

Aloisi, Gian Gaetano; Favaro, Gianna; Spalletti, Anna; Cavicchio, AU Giancarlo; Marchetti, Valeria

CS Dip. Chim., Univ. Perugia, Perugia, I-06100, Italy

Gazzetta Chimica Italiana (1986), 116(6), 281-4

CODEN: GCITA9; ISSN: 0016-5603

DT Journal

ĽΑ English

CC 22-7 (Physical Organic Chemistry) Section cross-reference(s): 52

Four 1- and 2-naphthyl esters of norbornadienecarboxylic acid and AB norbornadienedicarboxylic acid were prepared and the direct and sensitized photoisomerization studied. Direct irradiation of the esters gave several products, among which quadricyclane was present in a minor amount The benzophenone-sensitized irradiation was clean and high efficient to give quadricycling esters. The relatively high quantum yield for the photoreaction sensitized by the low energy donor by acetyl may also indicate a mechanism involving formation of a charge-transfer complex.

ST norbornadienecarboxylate naphthyl prepn photoisomerization; isomerization

```
photochem sensitized norbornadienedicarboxylate; quadricyclane
IT
     Isomerization
        (photochem., of naphthyl norbornadienecarboxylates)
IT
     698-40-8
               15872-28-3
     RL: RCT (Reactant); RACT (Reactant or reagent)
     (esterification of, with naphthols)
100641-65-4P 108164-78-9P 108164-81-4P 108164-82-5P
IT
     RL: PRP (Properties); SPN (Synthetic preparation); PREP (Preparation)
        (preparation and UV spectrum of)
IT
     108164-79-0P 108164-80-3P
     RL: SPN (Synthetic preparation); PREP (Preparation)
        (preparation and photoisomerization of)
     108164-82-5P
IT
     RL: PRP (Properties); SPN (Synthetic preparation); PREP (Preparation)
        (preparation and UV spectrum of)
     108164-82-5 HCAPLUS
RN
     Tetracyclo[3.2.0.02,7.04,6]heptane-1,5-dicarboxylic acid,
CN
```

di-2-naphthalenyl ester (9CI) (CA INDEX NAME)

ANSWER 20 OF 27 HCAPLUS COPYRIGHT 2004 ACS on STN

L49

os GI

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AN
     1986:109280 HCAPLUS
DN
     104:109280
     Entered STN: 05 Apr 1986
ED
     Naphthyl norbornadienecarboxylate.
ΤI
PA
     Dainippon Ink and Chemicals, Inc., Japan; Kawamura Physical and Chemical
     Research Institute
so
     Jpn. Kokai Tokkyo Koho, 5 pp.
     CODEN: JKXXAF
DT
     Patent
     Japanese
     ICM C07C069-753
IC
     ICS C09K005-00; F24J002-34
     25-24 (Benzene, Its Derivatives, and Condensed Benzenoid Compounds)
CC
     Section cross-reference(s): 52
FAN.CNT 1
                                DATE
                                            APPLICATION NO.
                                                                    DATE
     PATENT NO.
                         KIND
                         ____
                                                                    19831207
                                19850702
                                            JP 1983-229758
                         A2
PΙ
     JP 60123449
PRAI JP 1983-229758
                                19831207
CLASS
 PATENT NO.
                 CLASS PATENT FAMILY CLASSIFICATION CODES
                 _---
                        C07C069-753
                 ICM
 JP 60123449
                 ICS
                        C09K005-00; F24J002-34
     CASREACT 104:109280
```

AB Title compound I, useful as a light energy-converting substance, was prepared by Diels-Alder reaction of II (R = COC.tplbond.CH) (III) with cyclopentadiene (IV). I may also be prepared by esterification of II (R = H) with 2-norbornadienecarboxylic acid. Thus, stirring III and IV in AcoEt at room temperature for 20 h gave 76.7% I, which was isomerized to V by solar irradiation for 1 h. ST naphthalene norbornadienecarbonyloxy solar energy storage; light energy conversion norbornadienylcarbonyloxynaphthalene; solar energy conversion norbornadienylcarbonyloxynaphthalene; propioloyloxynaphthalene Diels Alder cyclopentadiene; quadricyclanecarboxylate naphthyl solar energy storage; photoisomerization naphthyl norbornadienecarboxylate solar storage; isomerization photochem norbornadienecarboxylate solar storage IT Isomerization (photochem., of norbornadienylcarbonyloxynaphthalene to quadricyclane derivative) IT Energy (solar, conversion of, naphthyl norbornadienecarboxylate for) IT Energy (solar, conversion of, naphthyl norbornadienecarboxylate isomerization in relation to) IT 91805-17-3

RL: RCT (Reactant); RACT (Reactant or reagent) (Diels-Alder reaction of, with cyclopentadiene)

542-92-7, reactions

RL: RCT (Reactant); RACT (Reactant or reagent)

(Diels-Alder reaction of, with propioloyloxynaphthalene)

IT 471-25-0

RL: RCT (Reactant); RACT (Reactant or reagent)

(esterification of, with hydroxynaphthalene, propioloyloxynaphthalene

from)

TT 698-40-8

RL: RCT (Reactant); RACT (Reactant or reagent)

(esterification of, with naphthol)

IT 135-19-3, reactions

RL: RCT (Reactant); RACT (Reactant or reagent)

(esterification of, with norbornadienecarboxylic acid)

IT 100641-66-5P

RL: FORM (Formation, nonpreparative); PREP (Preparation)

(formation of, by photoisomerization of norbornadiene derivative)

100641-65-4P IT

RL: SPN (Synthetic preparation); PREP (Preparation)

(preparation of, as light energy-converting substance)

ΙT 100641-66-5P

RL: FORM (Formation, nonpreparative); PREP (Preparation)

(formation of, by photoisomerization of norbornadiene derivative)

RN 100641-66-5 HCAPLUS

CN Tetracyclo [3.2.0.02,7.04,6] heptane-1-carboxylic acid, 2-naphthalenyl ester (CA INDEX NAME)

Kumar 10/612609

Page 45

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ANSWER 21 OF 27 HCAPLUS COPYRIGHT 2004 ACS on STN
     1984:191026 HCAPLUS
AN
DN
     100:191026
ED
     Entered STN: 08 Jun 1984
ΤI
     Photoelectron spectra and conformational behavior of azines
ΑU
     Kirste, Karl; Poppek, Rainer; Rademacher, Paul
     Inst. Org. Chem., Univ. Essen-GHS, Essen, D-4300, Fed. Rep. Ger.
CS
SO
     Chemische Berichte (1984), 117(3), 1061-8
     CODEN: CHBEAM; ISSN: 0009-2940
DT
     German
LΑ
CC
     22-3 (Physical Organic Chemistry)
GI
     For diagram(s), see printed CA Issue.
     The conformations of RRIC:NN:CRR1 (I; R, R1 = H, H; H, Me; H, Et; Me, Me;
     Et, Et; Et, Pr) and cyclic azines II (n = 3-6) and III were determined from
     their photoelectron spectra, and the interactions between the n and .pi.
     orbitals was examined by MNDO calcns. on I (R = R1 = H). The
     .pi.-ionization potentials of I, II, and III indicated s-trans
     conformations; the n ionization were of limited value.
     conformation azine photoelectron spectra; ionization potential azine
     conformation; MO interaction azine conformation
IT
     Azines
     RL: PRP (Properties)
        (conformation of, photoelectron spectra in relation to)
IT
     Energy level
        (correlation diagram, for azines)
TΤ
     Ionization potential and energy
     Molecular orbital
     Photoelectric emission
        (of azines)
IT
     Conformation and Conformers
        (of azines, photoelectron spectra in relation to)
     503-27-5 592-56-3 627-70-3 1530-17-2 4278-87-9
                                                             15601-98-6
     20615-04-7 24214-70-8 47180-21-2 72593-07-8 76924-71-5
     RL: PRP (Properties)
        (conformation of, photoelectron spectrum in relation to)
IT
     2053-29-4
     RL: PRP (Properties)
        (energy level correlation diagram for)
     47180-21-2
IT
     RL: PRP (Properties)
        (conformation of, photoelectron spectrum in relation to)
     47180-21-2 HCAPLUS
    Bicyclo[2.2.1]heptan-2-one, 1,7,7-trimethyl-, (1,7,7-
     trimethylbicyclo[2.2.1]hept-2-ylidene)hydrazone (9CI) (CA INDEX NAME)
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ANSWER 22 OF 27 HCAPLUS COPYRIGHT 2004 ACS on STN
L49
     1983:197655 HCAPLUS
AN
DN
     98:197655
ED
     Entered STN: 12 May 1984
     Polyfluorobicyclo[2.2.1]heptanes. Part XII. 4H-
     Decafluorobicyclo[2.2.1]hept-1-yl isocyanate, amine and alcohol, and
     derivatives therefrom
AU
     Broughton, John S.; Lynch, Peter; Stephens, Robert; Tatlow, John Colin
     Chem. Dep., Univ. Birmingham, Birmingham, B15 2TT, UK
CS
     Journal of Fluorine Chemistry (1983), 22(2), 123-32
SO
     CODEN: JFLCAR; ISSN: 0022-1139
DT
     Journal
LА
     English
CC
     24-7 (Alicyclic Compounds)
os
     CASREACT 98:197655
GI
```

Acid chloride I (R = ClCO) gave the corresponding isocyanate which readily afforded appropriate derivs. of carbamic acid, and substituted ureas I (R = PrO2CNH, PhNHCONH, etc.), all with the bridgehead moiety substituted on N. The 4H-bridgehead primary amine was made from the isocyanate and directly from the acid chloride. Diazotization converted it mainly to the bridgehead tertiary alc., with traces of the derived nitrite ester, and of the bridgehead chloride and dihydro compound Peroxide oxidation of the amine gave the bridgehead nitro compound fluorobicycloheptanecarbonyl chloride substitution nucleophilic; fluorobicycloheptyl isocyanate amine alc carbamate IT Substitution reaction, nucleophilic (of decafluorobicycloheptencarbonyl chloride) IT 74428-15-2 RL: RCT (Reactant); RACT (Reactant or reagent) (nucleophilic substitution of) 85670-38-8P IT RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent) (preparation and diazotization of) 85670-39-9P RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent) (preparation and esterification of) 85670-40-2P 85670-41-3P 85670-42-4P 85670-43-5P 85670-44-6P 85670-47-9P 85670-45-7P 85670-46-8P 85670-48-0P 85670-49-1P 85670-50-4P RL: SPN (Synthetic preparation); PREP (Preparation) (preparation of) 85670-44-6P RL: SPN (Synthetic preparation); PREP (Preparation) (preparation of) RN 85670-44-6 HCAPLUS Bicyclo[2.2.1]heptane-1-carboxylic acid, 2,2,3,3,5,5,6,6,7,7-decafluoro-,

GI

ANSWER 23 OF 27 HCAPLUS COPYRIGHT 2004 ACS on STN L49 AN 1978:104814 HCAPLUS DN 88:104814 ED Entered STN: 12 May 1984 Photolysis of 2-oxo-2,5-dihydro-1,3,4-oxadiazoles in the presence of ΤI olefins ΑIJ Daniil, Dimitra; Meier, Herbert CS Inst. Org. Chem., Univ. Tuebingen, Tuebingen, Fed. Rep. Ger. Tetrahedron Letters (1977),  $(3\overline{6})$ , 3155-8 SO CODEN: TELEAY; ISSN: 0040-4039 DТ Journal LΑ German CC 25-5 (Noncondensed Aromatic Compounds) Section cross-reference(s): 24, 28

2-naphthalenyl ester (9CI) (CA INDEX NAME)

The title oxadiazoles, prepared by cyclization of ketone semicarbazones, on irradiation in the presence of .alpha.-methylstyrene gave .alpha.-styrylmethyl hydrazones, parent ketones, and in some cases a sym. azine. E.g. oxadiazole I gave 64% hydrazone II, 30% azine III, and 6% adamantanone. Photolysis in the presence of cyclohexene gave a similar mixture of ST oxadiazole olefin photolysis; hydrazone styrylmethyl; cyclohexenyl hydrazone IT Photolysis (of oxadiazoles, in presence of olefins) IT10281-41-1 65814-27-9 RL: RCT (Reactant); RACT (Reactant or reagent) (cyclization of, oxadiazole derivative from) 110-83-8, reactions IT 25013-15-4 RL: RCT (Reactant); RACT (Reactant or reagent) (photochem. reaction of, with oxadiazoles) IT 39930-75-1 RL: RCT (Reactant); RACT (Reactant or reagent) (photolysis of, with cyclohexene) IT 28873-61-2 RL: RCT (Reactant); RACT (Reactant or reagent) (photolysis of, with methylstyrene and cyclohexene) IT 65814-39-3P 65814-40-6P RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent) (preparation and dimerization of) IT 65814-28-0P 71927-66-7P RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent) (preparation and photolysis of, with olefins) IT 65814-30-4P RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent) (preparation and reaction of, with ketones) 20615-04-7P 39555-34-5P 47180-21-2P 65814-31-5P 65814-33-7P 65814-32-6P 65814-34-8P 65814-35-9P 65814-37-1P 65814-38-2P 71927-67-8P RL: SPN (Synthetic preparation); PREP (Preparation) (preparation of) IT 3360-54-1 RL: RCT (Reactant); RACT (Reactant or reagent) (reaction, with hydrazine) ΙT 47180-21-2P RL: SPN (Synthetic preparation); PREP (Preparation) (preparation of) RN 47180-21-2 HCAPLUS Bicyclo[2.2.1]heptan-2-one, 1,7,7-trimethyl-, (1,7,7-CN trimethylbicyclo[2.2.1]hept-2-ylidene)hydrazone (9CI) (CA INDEX NAME)

```
1976:477307 HCAPLUS
AN
    85:77307
DN
ED
     Entered STN: 12 May 1984
    Thermal and photochemical decomposition of dihydrooxadiazinones
TI
     Fuchs, B.; Kwalwasser, W. D.; Rosenblum, M.
AU
CS
    Dep. Chem., Brandeis Univ., Waltham, MA, USA
     Israel Journal of Chemistry (1976), Volume Date 1975, 13(2), 107-24
     CODEN: ISJCAT; ISSN: 0021-2148
DT
    Journal
T.A
    English
CC
    22-7 (Physical Organic Chemistry)
```

IT

286-20-4 10373-78-1

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3,6-Dihydro-1,3,4-oxadiazin-2-ones [I; R = Ph, Me; R1 = Ph, Me; RR1 =
     (CH2)n, n = 6-8; R2 = H, Me, R1R2 = (CH2)5], prepared from either
     .alpha.-ketols or from .alpha.-diketones and carbethoxyhydrazine, undergo
     thermal or photolytic (253.7 nm) decomposition to give N2, CO2 and olefins.
     Oxadiazinones derived from medium ring .alpha.-ketols give bicyclic hydrocarbons in addition to olefins. These are formed by decomposition of the
     intermediate vinyldiazene to vinyl radicals, followed by transannular H
     abstraction and alkyl radical addition to the olefin. A series of
     5,6-dihydro-1,3,4-oxadiazin-2-ones are also prepared and their thermal and
     photolytic behavior studied.
     thermolysis photolysis dihydrooxadiazinone; hydrooxadiazinone thermolysis
     photolysis; oxadiazinone dihydro thermolysis photolysis
IT
     Photolysis
        (of dihydrooxadiazinones)
IT
     4233-33-4
     RL: RCT (Reactant); RACT (Reactant or reagent)
        (oxidation of oxadiazinones by)
IT
     60110-50-1P
     RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT
     (Reactant or reagent)
        (preparation and oxidation of)
     60110-49-8P
     RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT
     (Reactant or reagent)
        (preparation and reaction with phenyldehydrourazole)
     60110-44-3P
     RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT
     (Reactant or reagent)
       (preparation and reaction with sodium borodeuteride)
     60110-43-2P
     RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT
     (Reactant or reagent)
        (preparation and reduction of)
IT
     60110-47-6P
     RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT
     (Reactant or reagent)
        (preparation and ring closure of)
     60110-45-4P
                   60110-48-7P
                                  60110-51-2P
                                                60110-55-6P
     60110-57-8P
                    60134-24-9P
     RL: SPN (Synthetic preparation); PREP (Preparation)
        (preparation of)
                   60134-25-0P
     60110-58-9P
     RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT
     (Reactant or reagent)
        (preparation, photolysis, and thermolysis of)
     7506-24-3P
                  19836-49-8P 19836-51-2P 19836-52-3P 60110-46-5P 60110-52-3P 60110-53-4P
                                                               19836-54-5P
     60110-42-1P
                                                                60110-54-5P
     60136-52-9P
     RL: SPN (Synthetic preparation); PREP (Preparation)
        (preparation, thermolysis, and photolysis of)
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RL: PRP (Properties)
        (reaction with carbethoxyhydrazine)
     60110-59-0
    RL: PRP (Properties)
        (reaction with sodium borodeuteride)
TT
     4114-31-2
    RL: RCT (Reactant); RACT (Reactant or reagent)
        (reactions of)
IT
     60110-57-8P
    RL: SPN (Synthetic preparation); PREP (Preparation)
        (preparation of)
RN
     60110-57-8 HCAPLUS
CN
    Bicyclo [2.2.1] heptan-2-one, 4,7,7-trimethyl-, (4,7,7-
    trimethylbicyclo[2.2.1]hept-2-ylidene)hydrazone (9CI)
                                                             (CA INDEX NAME)
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ANSWER 25 OF 27 HCAPLUS COPYRIGHT 2004 ACS on STN
ΑN
     1969:512901 HCAPLUS
DN
     71:112901
ED
     Entered STN: 12 May 1984
TI
     Reaction of 1,2- and 1,3-dicarbonyl compounds with 1,3-diamines: some new
     1,4-diazepines
     McDougall, R. H.; Malik, S. H.
CS
     West Ham Coll. Technol., London, UK
SO
     Journal of the Chemical Society [Section] C: Organic (1969), (15),
     CODEN: JSOOAX; ISSN: 0022-4952
DT
     Journal
LA
     English
CC
     28 (Heterocyclic Compounds (More Than One Hetero Atom))
     CASREACT 71:112901
     Glyoxal sodium hydrogen sulfite addition compound reacts with
     2,4-diaminopentane dihydrochloride to yield 5,7-dimethylhexahydro-1,4-
     diazepin-2-one, but glyoxal monohydrate reacts with 1,3-diaminopropane and
     2,4-diaminopentane under alkaline conditions to produce more complex
     substances. Cyclohexane-1,2-dione condenses with 1,3-Diaminopropane to
     form 2,3,4,6,7,8-hexahydro-1H-1,5-benzodiazepine, but di-imines formed from two mols. of dicarbonyl compound and one of diamine result from the
     reactions of 1,3-diaminopropane with benzil, camphorquinone, and isatin.
     Complex products are obtained from o-quinones and diaminopropane.
     1,3-Diketones and 1,3-diamines react to produce open-chain compds. formed
     from two mols. of ketone and one of amine. 2,3-Dihydro-1H-1,4-diazepine
     is apparently formed from malonaldehyde and ethylenediamine, but
     1,2-diaminocyclohexane reacts with malonaldehyde to give
     1,2-bis(2-formylvinylamino)-cyclohexane.
     diazepines via diaminopentanes; diaminopentanes diazepines via
     82-86-0P 84-11-7P
                                                                  23927-23-3P
                           521-24-4P
                                        524-42-5P
                                                    2435-53-2P
                                  23927-61-9P 23927-62-0P
     23927-24-4P
                  23927-25-5P
     23954-20-3P
                   23954-21-4P
                                  23954-22-5P
                                                23954-23-6P
                                                               23954-24-7P
     23954-25-8P
                   23954-26-9P
                                  23954-27-0P
                                                23954-28-1P
     RL: SPN (Synthetic preparation); PREP (Preparation)
        (preparation of)
IT
     23927-62-0P
     RL: SPN (Synthetic preparation); PREP (Preparation)
        (preparation of)
RN
     23927-62-0 HCAPLUS
     Bicyclo[2.2.1]heptan-2-one, 3,3'-(1,3-propanediyldinitrilo)bis[1,7,7-
CN
     trimethyl-, [1.alpha.,3(1'R*,4'S*),4.alpha.]-(+)- (9CI) (CA INDEX NAME)
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Me 
$$N \leftarrow (CH_2)_3 - N \rightarrow Me$$
 Me  $Me$ 

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1963:8405 HCAPLUS AN DN 58:8405 OREF 58:1326c-h,1327a-d ED Entered STN: 22 Apr 2001 Reactions of the 2-bornyl radical. II. A free radical Wagner-Meerwein TI rearrangement Berson, Jerome A.; Olsen, Carl J.; Walia, Jasjit Singh CS Univ. Southern California, Los Angeles Journal of the American Chemical Society (1962), 84, 3337-48 SO CODEN: JACSAT; ISSN: 0002-7863 DT Journal Unavailable LΑ 32 (Physical Organic Chemistry) CC cf. CA 57, 11240.degree.. Racemic 2-azobornane (I), m. 164-5.degree. AB (N-filled capillary), was prepared from racemic camphor azine (II), m. 186-7.5.degree., by H-Pt reduction followed by KMnO4 oxidation of the initial 2-hydrazobornane (III). The azo link in I is probably trans, with the exo configuration at C-2. I, a convenient source of the 2-bornyl radical (IV), readily decomposed above 250.degree. in hexadecane (V) or Ph20. volatile products were removed in a vacuum line and the fraction passing a trap at 0.degree., containing 97% of the hydrocarbon products up to and including C10 fragments, was analyzed by gas chromatography. Decomposition in V yielded fragments from both solvent and I; all normal alkanes from C1 to C10 were identified. Olefins in the decomposition products were removed by percolation of a pentane solution of the volatile fraction through SiO2 gel. The identity of the products was established by comparison of the order of emergence and retention times on 4 different columns, by chromatography with authentic samples, by their chemical nature, and by preparative scale gas chromatography followed by infrared analysis. The products identified include bornane (VI), 1-p-menthene (VII), tricyclene (VIII), bornene (IX), and 2,3,3-trimethylnorbornane (isocamphane) (X), the Wagner-Meerwein rearrangement product. VII was apparently formed by .beta.-elimination from IV, with cleavage of the C1-C7bond, followed by H abstraction. .beta.-Elimination with cleavage of the C1-C6 bond would give RCH2CH2.bul. (R = 2,2,3-trimethyl-3-cyclopentyl) (XI) which, by H abstraction, would yield 1,5,5-trimethyl-4-ethylcyclopentene (XII). XII, b43 68-8.5.degree., n25D 1.4429, which was not isolated although evidence for its presence was obtained, was prepared from campholenealdehyde [(2,2,3-trimethyl-3cyclopentenyl)acetaldehyde] (XIII) in 88% yield by Huang-Minlon reduction, and in 49% yield by the Cook-Linstead modification of the Wolff-Kishner reduction XIII (45.6 g.) and 7.5 g. N2H4.H2O in 50 ml. EtOH left 12 hrs. at room temperature, poured into H2O, and the mixture worked up through Et2O gave yellow XIII azine (XIV), b1.5 164-6.degree., n25D 1.5028, .lambda.alc.maximum 206 m.mu. (log .epsilon. 4.37). To a stirred solution of 7.0 g. LiAlH4 in 50 ml. Et20 was added, dropwise over 30 min., 24.4 g. XIV in 50 Ml. Et20, the mixture stirred 12 hrs. at room temperature, cooled in ice, treated with 50 ml. cold 28% KOH, the Et2O layer removed, and the aqueous phase washed with Et2O. The combined Et2O solns. gave 89% hydrazo compound, b1 165-70.degree., which was dissolved in 25 ml. dry Et20, stirred 5 hrs. with 34 g. yellow HgO, 10 q. anhydrous Na2SO4, and 100 ml. Et2O, the mixture filtered through kieselguhr, the solvent evaporated under N, and the residue distilled to give 65% 1-azobis-2-(2,2,3-trimethyl-3-cyclopentenyl)ethane (XV), b1.5 149-54.degree.. Redistn. gave pure XV, b1.5 150-2.degree., n25D 1.4858, .lambda.maximum 207, 360 m.mu. (log .epsilon. 3.88, 1.47). Decomposition of XV, under the same conditions as for I, generated XI from which was obtained a mixture of products containing X and VI-IX. XI is thus the probable intermediate in the formation of X. X, from either I or XV, is a 3:1 mixture of stereoisomers in which the major component probably has the endo configuration at the lone Me group. The distribution of products under various reaction conditions is tabulated. H abstraction from I and XV, especially when the initial concentration was high, and from V was observed. A possible mechanism for the formation of VIII is an intramol. carbeneolefin addition from XI. In some decompns. NH3 was formed. At low initial concns. of I and XV the decomposition kinetics are first order; the kinetic data are tabulated. The decomposition of I was affected by trace impurities and with some solvent batches little or no N was evolved. This reaction is suggested as an impurity-catalyzed disproportionation of I, or the isomeric camphor 2-bornylhydrazone (XVI), to II and III. II was found in the non-volatile residues together with some I (possibly regenerated from the readily oxidized III). XVI, m. 180-80.5.degree. (N-filled capillary) (95% EtOH), was prepared in 79% yield by refluxing, for 12 hrs. under N, 30 ml. EtOH containing 3.0 g. camphor, 2.6 g. NaOAc, 15 ml. H2O, and 1.8 g. racemic 2-bornylhydrazine hydrochloride, m. 251-2.degree. (decomposition),

ANSWER 26 OF 27 HCAPLUS COPYRIGHT 2004 ACS on STN

L49

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(prepared by H-Pt reduction of racemic camphor acetylhydrazone, m.
189-90.5.degree., followed by treatment of the product with dry HCl). XVI
reduced by H-Pt and the product oxidized with KMnO4 in Me2CO gave I. The
reactivities of I and XV are normal since the rate consts. and activation
parameters for their decompns. are close to those for simple azoalkanes
(although the latter were decomposed in the gas phase). I is approx. 4 times as active as azoisopropane and XV is 6-7 times as active as
azoethane. It is considered unlikely that bond delocalization in the
alkyl groups of the azo compds. plays a significant role in the transition
state that leads to loss of N, and unlikely that a mesomeric radical is
the only intermediate in the Wagner-Meerwein rearrangement. H abstraction
appears to be sterically rather than stereoelectronically controlled and
the radical system gives more secondary product, VI, than tertiary, X.
Thus, there is no analogy between the behavior of cations and radicals in
the bornyl system. Part of the rearrangement may involve mesomeric
intermediates but it is not the exclusive path; a major portion passes
through classical radicals. This is compatible with the
non-stereospecificity of H capture, the absence of rate enhancement in the
azo decompns., and the dependence of the product composition on the source of
the radicals, and also explains the absence of rearrangement and
ring-opening when IV is generated at lower temps. since the cleavage step
will have a high activation energy. 37 references.
Spectra, visible and ultraviolet
   (of 1,1-azobis[2-(2,2,3-trimethyl-3-cyclopentenyl)ethane])
Activation energy, Heat of activation
Frequency factor, Preexponential factor
   (of 2,2'-azobornane decomposition by heat)
Wagner-Meerwein rearrangement
   (of 2-bornyl radical)
Entropy
   (of activation of 2,2'-azobornane by heat)
Reaction kinetics and (or) Velocity
   (of decomposition, of 2,2'-azobornane and 2,2'-bis(2,2,3-trimethyl-3-
   cyclopenten-1-yl)azoethane by heat)
Mass spectroscopy
   (of solids)
2,2'-Azobomane
                    464-17-5, 2-Bornene 473-19-8, Norbornane,
464-15-3, Bornane
                   508-32-7, Tricyclo[2.2.1.02,6] heptane, 1,7,7-trimethyl-
2.2.3-trimethvl-
5502-88-5, p-Menth-1-ene
   (formation in 2,2'-azobornane decomposition)
47180-21-2, Camphor, azine 52491-59-5, Cyclopentene,
4-ethyl-1,5,5-trimethyl- 90976-37-7, Cyclopentane, 1-chloro-3-ethyl-
                              91087-16-0, 3-Cyclopentene-1-acetaldehyde,
94676-28-5, Hydrazine, 1,2-bis[2-(2,2,3-
1,2,2-trimethyl-5-nitroso-
2,2,3-trimethyl-, hydrazone
trimethyl-3-cyclopenten-1-yl)ethyl]- 94681-90-0, 3-Cyclopentene-1-acetaldehyde, 2,2,3-trimethyl-, azine 95389-88-1, Hydrazine,
(2-bornyl)-, hydrochloride 95706-56-2, Azoethane, 2,2'-bis(2,2,3-
trimethyl-3-cyclopenten-1-yl) - 101700-26-9, Camphor, 2-bornylhydrazone
135866-41-0, Acetic acid, 2-bornylidenehydrazide
   (preparation of)
118659-24-8, 2-Bornyl
   (reactions of)
47180-21-2, Camphor, azine
   (preparation of)
47180-21-2 HCAPLUS
Bicyclo [2.2.1] heptan-2-one, 1,7,7-trimethyl-, (1,7,7-
trimethylbicyclo[2.2.1]hept-2-ylidene)hydrazone (9CI)
                                                          (CA INDEX NAME)
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IT

IT

IT

IT

ΙT

IT

IT

RN CN

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L49 ANSWER 27 OF 27 HCAPLUS COPYRIGHT 2004 ACS ON STN AN 1937:61827 HCAPLUS DN 31:61827 OREF 31:8526f-i ED Entered STN: 16 Dec 2001
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Kumar 10/612609

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the ketazines of camphor and carvomenthone
AU
     Taipale, K. A.; Gutner, M. A.; Remiz, E. K.
so
     Zhurnal Obshchei Khimii (1937), 7, 1378-89
     CODEN: ZOKHA4; ISSN: 0044-460X
DΤ
     Journal
     Unavailable
LΑ
     10 (Organic Chemistry)
CC
     cf. C. A. 25, 2415. The ketazine of carvomenthone is hydrogenated 5 times
     faster than that of camphor over Pt black. Thus, the formation of the
     camphane bridge strongly raises the affinity capacity of the alicylic
     ring. The hydrogenation products are the symmetrically disubstituted
     hydrazines. Camphor ketazine gives 2-hydrazocamphane (I) m.
      135-6.degree. In air, this partly oxidizes to azocamphane (II), but the
     latter is better prepared by oxidizing I with KMnO4 or H2O2. I forms a
     monohydrochloride, m. 235.degree. (decomposition), and a mono-Bz derivative m. 137-8.degree. II, m. 148-9.degree., [.alpha.]D19 -59.44.degree., is isomerized by HCl to C10H17NHN:C10H16.HCl, m. 200.degree. (decomposition).
     More vigorous treatment with HCl gives camphor and bornylhydrazine.
     Attempts to isolate the free base lead to tar formation.
IT
     Azines
         (hydrogenation of)
IT
     Hydrogenation
         (of azines)
     Benzoic acid, 1,2-dibornylhydrazide Camphane, 2,2'-azodi-
IT
     Camphane, 2,2'-hydrazodi-
     Camphane, 2,2'-hydrazodi-, -HCl
     Camphane, 2-hydrazino-
     Camphor, bornylhydrazone-HCl
     Hydrazine, 1,2-dibornyl-
     Hydrazine, 1,2-dibornyl-, -HCl
Hydrazine, bornyl-
ΙT
     Carvomenthone, azine
         (hydrogenation of)
IT
     47180-21-2, Camphor, azine
         (hydrogenation of)
IT
      47180-21-2, Camphor, azine
         (hydrogenation of)
     47180-21-2 HCAPLUS
RN
     Bicyclo [2.2.1] heptan-2-one, 1,7,7-trimethyl-, (1,7,7-
CN
```

trimethylbicyclo[2.2.1]hept-2-ylidene)hydrazone (9CI) (CA INDEX NAME)

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=> b home FILE 'HOME' ENTERED AT 14:37:53 ON 10 DEC 2004